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Synthesis and Characterization of Platinum (II) Complexes with Thiophene-Based Ligands

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SYNTHESIS AND CHARACTERIZATION OF PLATINUM(II) COMPLEXES WITH THIOPHENE-BASED LIGANDS

Senior Project Submitted to
The Division of Science, Mathematics, and Computing at Bard College

by
Julienne Sarabia
Class of 2015



Annandale-on-Hudson, New York
May 2015

I would like to dedicate this project to my beloved grandmother, Lorna T. Aldeano. How I wish you could have been here to celebrate this milestone in my life.

Love you always and rest in peace.

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Abstract:

Multi-dentate thiophene-derived imine ligands, with a cyclohexyl backbone containing a variety of stereocenters, were synthesized and then subsequently reacted with the binuclear platinum compound, $[\text{Pt}_2\text{Me}_4(\mu\text{-SMe}_2)_2]$, to afford cyclometalated platinum(II) species with C[^]N[^]N pincer-type ligands. The complexes were characterized by NMR, IR, UV/vis, and emission spectroscopy. The complexes' reactions with methyl iodide were explored to determine the stereospecificity of the oxidative addition reaction to form platinum(IV) species.

1. Introduction

I. A Survey on C-H Bond

In the study of chemistry, it is no contest that the carbon-hydrogen bond functionality is considered to be the simplest and most omnipresent motif. It can be essentially considered as the “un-functional” group, which simply refers to the fact that its presence in a molecule is an indication of the absence or lack of more useful bond functionality at that specific site.⁸ In spite of its simplistic and ubiquitous nature, carbon-hydrogen bonds, along with carbon-carbon bonds, in fact, are integral to the structures of larger and more complex molecules in that these bonds constitute their skeletal backbone. The structure of this backbone can greatly influence the arrangement and orientations of other bond functionalities with respect to one another thereby inherently influencing a compound’s chemical and physical properties. Additionally, with respect to the abundant presence of C-H bonds, functionalization of these bond moieties present alternate synthetic routes for the synthesis of larger, intricate compounds from simpler, more abundant, and cheaper precursors, like alkanes.^{1,2,6,7,8,12} Furthermore, because C-H bonds are one of the inextricable building blocks of complex macromolecules, its presence allows the possibility for further modifications and change. However, few pragmatic processes exist which allows for the direct conversion of carbon-hydrogen bonds into other bond functionalities.² With these ideas in mind, the study of C-H bond transformation into more chemically useful substrates presents a compelling basis for scientific inquiry.

Moreover, there also exists an economical and environmental demand for the development of novel and greener methods for the transformation of hydrocarbons into more useful materials for the specific purpose of augmenting and/or eventually displacing

petroleum as the source of liquid fuels and chemicals.^{2,7} At this time, most contemporary industrial methods employed for C-H functionalization are typically costly and environmentally unfriendly. Such processes generally involve the use of free radicals or carbocations and tend to require high reaction temperatures, essentially increasing cost and emissions of the process.^{1,2,7} Therefore, the development of innovative and selective reaction of C-H bonds is equally appealing from a practical viewpoint because such methods would, in theory, allow for the conversion of these bonds at remarkably milder conditions, higher rates, lower temperatures, and with much greater specificity when compared to classical methodology. Ultimately, the development of novel methods for C-H bond transformation would be of great benefit to chemical companies as it provides a cleaner and more cost-efficient alternative for C-H functionalization.

Prior to the advent of the discovery of C-H activation, the ubiquitous presence of C-H bonds proved to be quite the chemical conundrum for many chemists. In fact, their unreactive tendency is reflected in the vernacular terminology for alkanes: *paraffins*, which is derived from the Latin *parum affinis*, or “without affinity”.^{1,13} The fundamental basis of the difficulty of C-H functionalization is centered on the inert nature of the C-H bond.^{1,2,5,6,7,8,12,13,14} This chemical inertness is derived from the C-H bond’s relatively high bond energy, which ranges from 90 to 100 kcal/mol, as well as its relatively low acidity and basicity, which is supported by the low pK_a values (ranging from 45 to 60).¹⁴ Moreover, the C-H bond’s inertness also arises from the strong localization of C-C and C-H bonds within the respective saturated or unsaturated hydrocarbon molecule. As a result, hydrocarbons either do not have empty orbitals of low enough energy (as with the case of alkanes) or

filled orbitals of high energy (as with the case of unsaturated hydrocarbons) that could readily participate in a chemical reaction.²

Arguably, these factors suggest that hydrocarbons, in particular alkanes, can be considered to be the “noble gases of organic chemistry”. However, this comparison is in fact not necessarily accurate. While C-H bonds are, in fact, relatively inert, this does not automatically suggest that it does not undergo reaction.¹ In reality, hydrocarbons are capable of participating in chemical reactions, but they only do so at very harsh conditions. Alkanes, for example, do in fact react readily with oxygen at very high temperatures through deep oxidation, or combustion.^{1,2,5} Unfortunately, the combustion of alkanes is not a highly desirable process for many reasons. First, the reaction is not readily controllable and only exploits the energy content of the hydrocarbons to produce thermodynamically stable, but economically unattractive products: carbon dioxide and water.^{1,2,5}

Alkanes can also be functionalized via free radical mechanisms, as often observed with photochlorination and autoxidation.^{1,2,7} Nevertheless, free radical mechanisms are generally undesirable primarily because of the lack of selectivity of the reaction. It often results in the formation of many unwanted products. Consequently, this makes purification and resolution of your desired compounds difficult because of the formation of undesirable products and all possible isomeric configurations of the desired product(s). Other industrial methods also exist for the functionalization of C-H bonds, such as cracking and thermal dehydrogenation.² These techniques are mainly utilized to convert alkanes into more valuable olefins for further processing. However, these means of C-H transformation also require harsh conditions: high temperature and high pressures, and

are very energy intensive, which therefore makes the entire process quite costly for chemical industries.

Not all hydrocarbons are unreactive. Unlike their saturated counterparts, unsaturated hydrocarbons have greater potential to participate in a chemical reaction and be functionalized under milder conditions. This capability stems from the fact that these unsaturated systems have access to π electron and orbitals, which facilitate their ability to undergo addition/elimination reactions. However, the conversion of alkenes and alkynes are also fairly inefficient and also suffers from lack of selectivity when special catalytic reagents and conditions are not involved.⁶

Recent developments in the field of organometallic chemistry have given rise to transition metal mediated C-H activation to resolve the difficulty in C-H bond functionalization.^{1,2,5,6,7,8,12,13,14} In this process of C-H activation, the substrate is bound to a metal center, which can be followed by a subsequent functionalization step. The driving force that enables for the transformation of regularly inert C-H bonds is that ligand binding to a metal center changes the ligand's chemical and physical properties⁵. Consequently, this results in associated changes to the relative energies of the orbitals or molecule's polarity which ultimately alters or enhances the reactivity of the substrate bound to the metal center.^{1,2,5} Moreover, transition metal mediated pathways also offers an economic solution for the process. Transition metal mediated systems offer access to catalytic systems wherein the metal is regenerated and produces the desired product in large quantities for a small amount of catalyst. This possibility is inexpensive because it does not require large amounts of expensive reactants to produce the final functionalized product! Additionally, since the metal center behaves as a catalyst, it reduces the overall energy

requirement of the process—thereby reducing costs as a whole. Not only does this make the process economically feasible, it also allows for a cleaner means for C-H functionalization as it reduces chemical waste. Thus, a transition metal mediated pathway offers an ideal and logical methodology for C-H functionalization as it opens the possibility for more sensitive, selective, economic, and cleaner means to do so.

C-H activation allows for the functionalization of C-H bonds. This occurs through initial cleavage of the C-H bond and the resulting formation of a M-C σ bond, a bond that is more susceptible for functionalization than its previous counterpart.^{1,2,5,8} This new bond can then be easily and readily functionalized via reductive elimination with an adjacent ligand, which must also be bound to the metal center. The facile nature of this process has profound practical effects within the field of academics, as well as within chemical industry. It opens novel synthetic routes for the synthesis of larger and more complex molecules by allowing the use of simpler precursors, like alkanes. C-H activation also allows for the efficient production of important and vital chemicals, like fuels and plastics, from cheap, simple, and abundant starting materials.² Ultimately, this reduces production costs and minimizes the demand and use of liquid petroleum as feedstock for chemical industry.^{1,2,7}

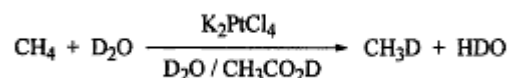
Despite the fact that the final functionalized derivatives themselves are of great importance and utility, the organometallic species are also of great interest to chemists for various reasons. Notably, these species possess catalytic capabilities which are greatly affected by changes in metal or ligand identity and ligand spatial orientation. Therefore, studies on their catalytic properties are also of great importance as it can be utilized to increase the efficiency of industrial methods of C-H activation. Additionally, the aforementioned modifications also have great influence on the organometallic complex's

reactivity and selectivity of the organometallic species' reaction with other substrates. This is vitally important to both academic and industrial syntheses in that the discovery of organometallic structures leading to selective functionalization of these bonds can greatly open more efficient routes for complex syntheses of vital stereospecific compounds.

II. *Roots of C-H Activation*

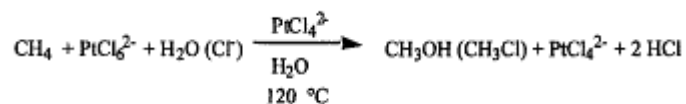
The first generally accepted report of C-H activation was attributed to Chatt's work in 1962 with the synthesis of $[\text{Ru}(\text{dmpe})_2]$. The Ru compound was reported to be behaving 'anomalously' because it showed an unprecedented $\nu(\text{Ru-H})$ signal in its IR spectrum, owing to the C-H activation of either a C-H bond within a ligand phosphinomethyl group or a C-H bond of naphthalene.⁸ Additionally, around the same time Chatt worked with ruthenium, Wilkinson's work with hydrogenation catalysis provided an example wherein the reductive elimination of a C-H bond was explicitly involved in the catalytic cycle.⁸ This promptly inspired Shilov to extend these ideas to platinum complexes, effectively demonstrating the possible application of Pt for the activation of C-H bonds.

Shilov's first work with C-H activation examined the Pt (II) mediated H/D exchange between methane and D_2O , shown below:



Equation 1: H/D exchange between methane and D_2O in the presence of Pt(II). Taken from Reference 8.

In 1972, he published a dramatic advance to this earlier report of C-H activation with Pt (II), wherein he added Pt(IV) to the aqueous reaction of PtCl_4^{2-} with methane. This addition led to the production of selectively oxidized species methanol and methyl chloride!⁸



Equation 2: Aqueous reaction of PtCl_4^{2-} and methane for the production of selectively oxidized methanol and methyl chloride in the presence of added Pt(IV). Taken from Reference 8.

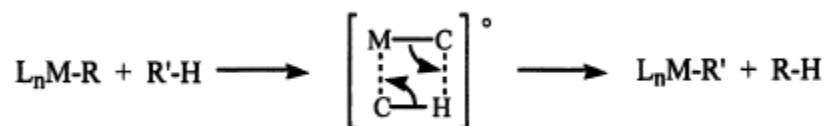
Despite the inherent implications of this transformation, the above reaction, given in Equation 2, poses an important issue: the reaction involving Pt(IV) is *stoichiometric*, while in the case of only the Pt (II) mediated reaction (given by Equation 1), the reaction is *catalytic*.⁸ While the Shilov system, which employs both Pt(II) and Pt(IV), allows for the selective functionalization of C-H bonds, the stoichiometric nature of the reaction is highly unfavorable and generally unwanted simply because it is impractical. Once Pt(IV) has served its part and is reduced, it is rendered useless within the reaction and cannot be reused for another round, which essentially wastes valuable and very expensive reagent⁸. In comparison, a catalytic cycle conserves the metal species, in this case Pt (II), for various cycles to obtain large amounts of final product for a small amount of given catalyst. Therefore, it is better for the reaction to be catalytic simply because it would mean expensive Pt metal does not have to be wasted and would be more efficient due to the “reusability” of the metal.

This, however, does not necessarily take away from the magnitude of Shilov’s findings. To date, the Shilov system remains today as one of the relatively few catalytic systems that can actually accomplish selective alkane functionalization under mild conditions.^{1,8} This distinction and the fact that it is one of the first few examples of such transformation justify its prominent status within the study of C-H activation. Interestingly, it is worth mentioning that this exciting discovery did not receive much attention from researchers outside the Soviet Union despite the fact that Shilov published

extensively on his system.⁸ It would not be until the 1980s that researchers would realize and grow aware of the importance of his work.^{1,2} Ten years after the renaissance of C-H activation, Labinger and Bercaw revisited Shilov's system and shed light into the mechanism of the Pt (II)/Pt (IV) mediated transformation of an alkane.^{2,8}

III. C-H Activation Reactions

Metal mediated activation and cleavage of C-H bonds can occur in various different fashions: sigma bond metathesis, 1,2 addition, radical pathways, and oxidative addition. Sigma bond metathesis involves the interchange of an existing sigma ligand bond via reaction with an incoming ligand's sigma bond (shown below).



Equation 3: General mechanistic scheme for σ -bond metathesis, where M=metal and R=alkyl group. Taken from Reference 8.

Often it occurs with alkyl or hydride complexes of 'early' transition metals with d^0 electronic configurations. It is mechanistically possible because it is stabilized by a four-membered transition state and always results in the formation of a M-R', not R-R', and R-H bond.^{2,8,26} Other means of C-H activation can occur via 1,2-addition, which are reactions that involve the addition of an alkane to a metal-nonmetal double bond. Unfortunately, the scope of this type of reaction is still rather unclear.² Activation can also occur via radical pathways, which are based upon porphyrin complexes of mainly Rh (III) and Ir (II). It suffices to say that such complexes can reversibly break alkane C-H bonds preferentially.² C-H activation can be classified as proceeding through electrophilic modes also.^{1,2,5,8}

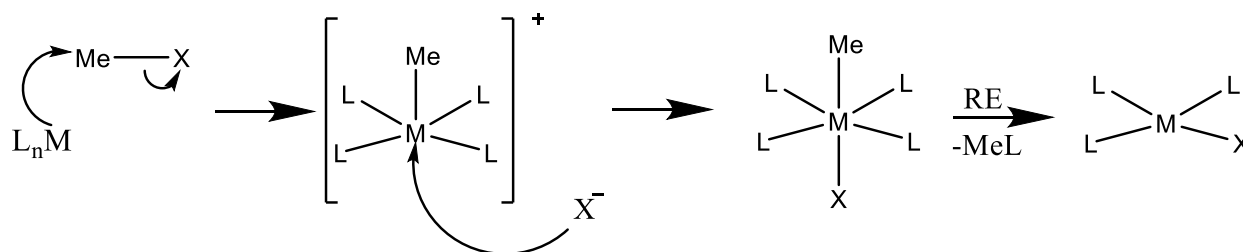
Electrophilic C-H activation is the class of reactions that do not necessarily lead to an observable organometallic species, although research strongly indicates their participation within the reaction as intermediates⁸. These class of reactions are typical of late- or post-transition metals, like $\text{Pd}^{2+}/\text{Pd}^{4+}$ and $\text{Pt}^{2+}/\text{Pt}^{4+}$, usually in strong polar mediums, like water or anhydrous strong acid.^{1,2,5,8}

In the scope of this study, however, C-H activation occurs mainly via oxidative addition (OA) pathways. As the name suggests, it involves the increase of both the formal oxidation state and coordination number of the metal. These reactions are typical for electron-rich, low-valent complexes of late transition metals, like Rh, Ir, and Pt.¹ OA reactions can be mechanistically categorized into the following subsets: concerted, $\text{S}_{\text{N}}2$ -type, and radical.^{1,2,5,8} Suffice to say, radical oxidative additions and free-radical mechanistic pathways are generally avoided because little is known about such pathways and results in the formation of many products.

Before talking in great detail about the mechanistic pathways for OA to occur, certain conditions must be met in order for the reaction to even take place. First, the metal complex must be coordinately unsaturated.^{5,8} This means that there must be space available for the addition of the substrate. OA will not occur if the metal center cannot accommodate the incoming ligand. Second and finally, the metal center must not be in its highest oxidation state.⁸ If a metal center is already in its highest oxidation state, it will not undergo OA because it cannot be further oxidized. Generally, the more reduced the metal center is, the more prone OA is likely to happen. Note, oxidative addition reactions are most facile when there is a good redox couple, which essentially means that the initial and

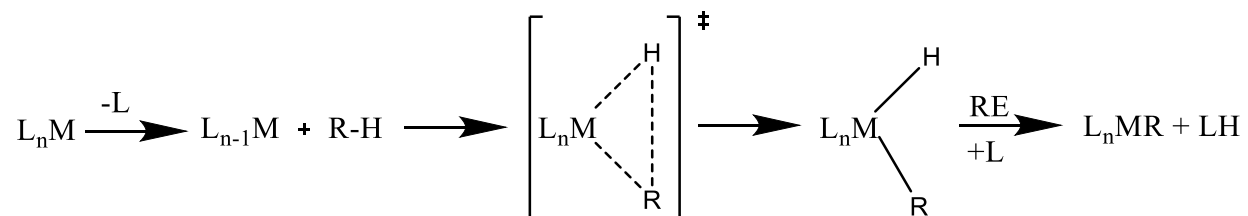
final oxidation states of the metal are relatively stable.^{1,2,5,8} If and only if these conditions are met, OA is likely to occur via either concerted or S_N2 type mechanism.

S_N2 type oxidative addition (OA) reactions usually take place with polar substrates, like alkyl halogens⁸. The mechanism is given below:



In this type of OA, the metal complex is electron rich due to the electron donating nature of the ancillary ligand, L. Appropriately, the metal behaves as a nucleophile and attacks the alkyl halogen in a fashion similar to that of the organic S_N2 reaction. The metal complex attacks the positive carbon center, causing the cleavage of a carbon-halogen bond and the formation of a five-coordinate complex from the original four-coordinate species. This change in coordination sphere during the formation of the intermediary species is important because it changes the geometry of the original metal complex from square planar to square pyramidal. Square pyramidal geometry, in fact, is prone to rearrangement, which may pose a problem for analysis. It is very likely that the complex can rearrange before the addition of X onto the metal complex and produce isomeric products⁵. In general, though, the defining characteristic of S_N2 OA is that the alkyl halide adds *trans* to each other on the organometallic complex and that the stereochemistry at the electrophile carbon center is inverted.^{5,8}

Concerted oxidative addition reactions, or three-centered OA reactions, are typical with most nonpolar substrates and follow the general mechanism shown below:



The hallmark characteristic distinguishing concerted OA from S_N2 is that the reaction results in the *cis* addition of the R-H bond to the metal complex.^{1,5,8} Concerted OA addition leads to the formation of a metalhydride complex. Unfortunately, such complexes are generally transient and unobservable due to their reactivity.^{3,9,10,26} But, there have been instances wherein the metal hydride complex is stable enough to be seen²⁸. After the OA step, the initial ligand, which dissociated earlier to allow for it to occur, reassociates. The sterics of the six-coordinate metal complex facilitates the reductive elimination (RE) of H and an adjacent ligand, L, giving the final organometallic product. Note, that there is competition for reductive elimination.

Cyclometalation, particularly *orthometalation*, is of great import within this particular study. It is the subset of OA that refers to the transition metal mediated activation of a C-R bond to form a metallacycle consisting of a new M-C σ bond.¹¹ The most common type of such reactions are known as *orthometalations*, and are so called because the OA occurs at the *ortho* position of an aromatic ring resulting in the linkage of that position to the metal center.¹¹ Orthometalations generically involve two steps. First, there is coordination of the metal center by way of donor groups, such as P or N, leading to the formation of a chelated metal complex, which simply means the ligand has multiple points of attachment to the metal. This chelation is integral to the second and final step: the intramolecular activation of the C-H bond, leading to the formation of a cyclic organometallic product.¹¹ Not only does chelation support the M-C bond, by way of the

electron donor groups, it facilitates the intramolecular OA by bringing the substrate in close proximity to the metal center.^{11,17} This makes the reaction more likely to occur as it reduces the enthalpic and entropic costs of the subsequent bond activation step and ring closure.¹¹

IV. *Factors Affecting Oxidative Addition*

As mentioned earlier, certain conditions must be fulfilled in order to resolve the steric and electronic changes necessitated by oxidative addition. With this in mind, the identity of the metal center becomes highly important as it is responsible for mediating the reaction. For the metal of choice to be an appropriate facilitator, it must be coordinately unsaturated. This means that the metal must have available coordination sites to which the substrate can oxidatively add.^{1,2,5,8} When the metal is coordinately saturated, OA cannot happen as a result of steric hindrance and a lack of free metal valence orbitals with which the substrate's C-H bond can interact with. Second, the metal of choice must not be in its highest oxidation state and must have access to an $n+2$ higher oxidation state. Lastly, the metal must be electronically unsaturated in order to accommodate the increase in electrons. Late transition metals, like Pt, Pd, Ru, and Ir, best satisfy these conditions and are therefore typically the metal of choice for such reactions.¹

Platinum, as it is the metal of choice in this study, has been repeatedly shown to facilitate C-H activation. Its common oxidation states are Pt (II) and Pt (IV), satisfying the need for a stable lower oxidation state and a stable $n+2$ higher oxidation state. Its valence electron count are 16 and 18 electrons, respectively, meaning that it can readily accommodate the two electron gain necessitated by oxidative addition. Lastly, in its 2+

oxidation state, Pt has a d^8 electronic configuration which takes a square planar geometry. This configuration is relatively coordinately unsaturated and can accommodate incoming substrates in the two vacant axial positions.

In addition to the identity of the metal center, C-H activation through cyclometalation is also largely impacted by the ligand environment of the metal center.¹¹ One important consideration to make is the identity of the donor group involved in the first step of the process. This initial chelation step, while it may seem a trivial process at first glance, can make the cyclometalation process more complex. The donor groups must match the hard-soft acid base principles. If the donor group and metal are mismatched, this may lead to difficulties in regioselectivity.¹¹ In the case of Pt, it is best to use soft Lewis bases in order for the cyclometalation to be successful. Ligand identity can also greatly affect the metal's electron density, and consequently its ability to react. Pt(II) complexes are most likely to undergo oxidative addition in electron rich environments. As such, electron donating atoms, like N or P, can be inserted into the ligand structure so as to increase electron density on the Pt center.¹¹ N atom containing ligands are of particular interest, in part because the ligands in the study are N-containing, but also because they are versatile. N donor ligands tend to have favorable electronic (strongly σ donating) and steric properties.¹⁷ In addition, the coordination of N to Pt, by virtue of the lone pair on N to form the C[^]N σ bond, enhances the nucleophilicity of Pt (II), ergo its reactivity and stabilizes the transient Pt (IV) species. When coupled to the fact that the Pt is brought into proximity to the thiophene by virtue of the N[^]Pt bond (Figure 1), it allows for the chelate assisted activation of the C_{sp}²-H bond through concerted OA.

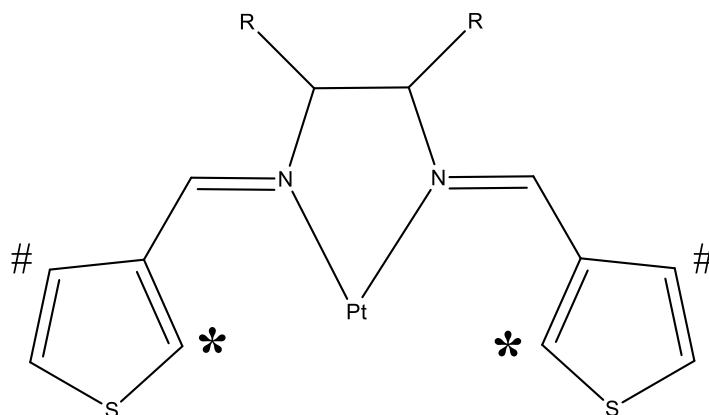


Figure 1: Generic multi-dentate thiophene di-iminic ligand formed after reaction of ligand with Pt-dimer. Note how the formation of the N[^]Pt σ bond brings it in close proximity to the C-H bond of the 2 position of the thiophene (as indicated by the asterisk). This close proximity by virtue of chelation is key to facilitating the concerted oxidative addition reaction. Position 4, indicated by # is also an ortho position.

This is supported by an earlier study by Anderson et. al with similarly constructed aryl-halide compounds. Their work proved that S_N2 type OA is not possible due to steric bulk of the ligand, which prevents nucleophilic attack, and low experimental ΔS^\ddagger values, which they believe did not indicate the type of highly ordered transition states typical for S_N2 type OA, which were often observed as large negative values.⁹

Ligand sterics must also be taken in to consideration as well because highly steric structures can make coordination difficult by preventing easy access to the metal center.^{5,11} Moreover, donor group sterics can either facilitate or hinder coordination.¹¹ Additionally, the identity of ancillary ligands are also of great importance. The reason for this is that, often, the chelation step is preceded by the transient dissociation of some labile ligand. If this bond is too strong and too stable, this reduces the labile nature of the ligand and reduces the likelihood of dissociation from the coordination complex.^{5,11} This would make chelation difficult as it requires empty coordination sites. If on the other hand the bond is

too weak, this can shift the equilibrium to the starting materials, preventing the formation of the chelated complex rendering the process more complex.¹¹

V. Research

Selective orthometalations of various functionalized multi-dentate thiophene-derived single iminic ligands have been greatly studied within the Anderson lab in the previous years. The structures of these aforementioned ligands have been shown to promote regioselective C-H activation at the 2 (*ortho*) position of the thiophene under mild conditions (Figure 2).^{3,4,9,10}

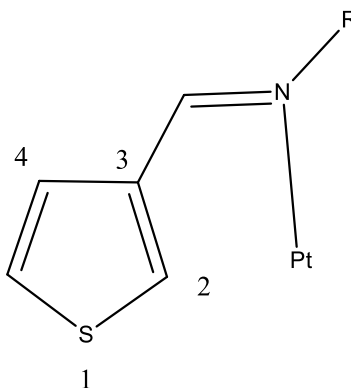


Figure 2: Generic structure of single iminic-thiophene ligand studied in the Anderson lab, with positions labeled. Coordination of $N^{\wedge}Pt$ brings it in close proximity to the 2 position of the thiophene, facilitating the C-H activation and subsequent cyclometalation at that spot.

According to Anderson et al., the selectivity of the C-H activation is a result of the steric and electronic factors intrinsic to the ligand structure.^{3,4,9,10} The activation of the C-H bond (position 2 or 4) adjacent to the imine moiety (position 3) is greatly favored because of the location of N with respect to the thiophene. As a result of coordination of Pt to N, Pt is brought in close proximity to the thiophene, which facilitates the activation at the two

ortho positions (2 or 4). Both locations are sterically viable for activation because the σ bond connecting the imine to the thiophene is free to rotate.^{3,4,9,10} Studies in the Anderson lab with thiophene-derived ligands, however, have been shown to favor position 2 over position 4. The reason being that position 2 is in closer proximity to the S atom, an electronegative atom. Sulfur's electronegative nature draws electron density from position 2, facilitating the subsequent intramolecular oxidative addition.^{3,4,9,10}

Stereoselectivity in organometallic reactions is of great import for many reasons. Studies in the Anderson lab thus far have extensively studied the reactivities, regioselectivity and stereoselectivity of only single iminic thiophene-derived ligands.³ Generic Pt (II) complexes previously synthesized by the Anderson lab typically contained a single imine moiety (Figure 2) were shown to react in a regioselective and stereoselective manner.^{3,4,9,10} The study, herein, is therefore interested in the synthesis, characterization, and reaction of stereoselective di-iminic thiophene-derived ligands

In order to study the stereoselective potential of these di-iminic thiophene-derived ligands, structural modifications to the general structure of imine thiophene-based ligands were made and modeled after a study by Baar et al. in 1998. This aforementioned study showed the propensity of diimine ligands, derived from chiral *cis*- or *trans*-diaminocyclohexane, to participate in very stereoselective oxidative addition reactions.^{18, 20,21,22,23,24} Appropriately, the thiophene ligands in the study incorporate the chiral cyclohexyl backbone with the hope of producing chiral ligands and Pt complexes (Figure 3).

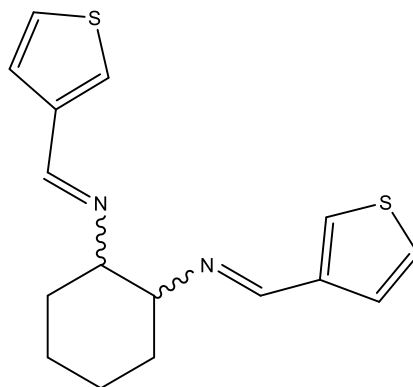


Figure 3: General structure of chiral multi-dentate thiophene-derived diiminic ligand with stereocenters at carbon 1 and 2 of the cyclohexyl ring.

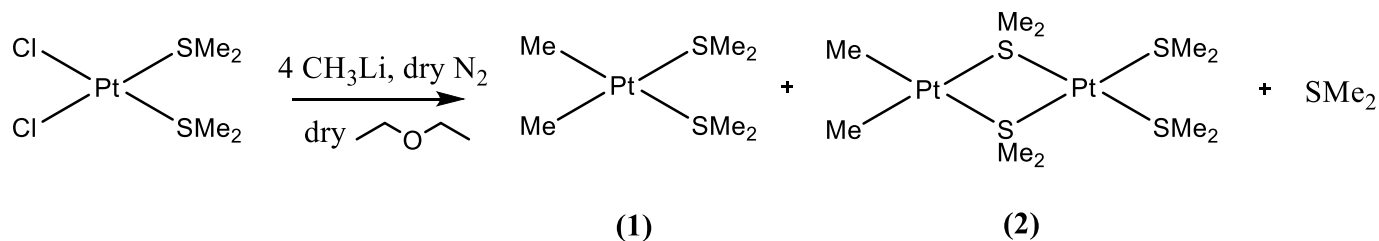
This chiral cyclohexyl backbone is the cornerstone to the stereoselectivity of the resulting Pt(II) complexes because chirality is induced into the organoplatinum (II) and organoplatinum (IV) species by virtue of the diimine chelates.^{18,20,21,22,23}

These subset of chiral di-iminic ligands present interesting features. As with previous Pt complexes containing thiophene ligands, these complexes may contain unique photophysical properties. However, their unique characteristic is that they possess a capability for stereoselective oxidative additions. Since oxidative addition is inherent and a key step in many catalytic processes, understanding the properties and characteristics of such stereoselective compounds can be of great benefit to the chemical industry because it allows for better understanding of chiral catalysis and the creation and design of the catalysts that mediate such reactions.

2. Results and Discussion

Full description of experimental synthetic procedures for all attempted syntheses of ligand and Pt complexes, can be found in the Experimental Section.

2.1 Synthesis and Characterization of $[\text{Pt}_2\text{Me}_2(\mu\text{-SMe}_2)_2]$



Scheme 1: The reaction for the synthesis of $[\text{Pt}_2\text{Me}_2(\mu\text{-SMe}_2)_2]$

$[\text{Pt}_2\text{Me}_2(\mu\text{-SMe}_2)_2]$, referred to in this work also as Pt-dimer and/or dimer, served as the Pt(II) starting material from which all Pt(II)-ligand complexes were derived and were previously synthesized and characterized in accordance with literature procedures.^{3,4} Precursor *cis/trans*- $[\text{PtCl}_2(\text{SMe}_2)_2]$, in the presence of methyl lithium, CH_3Li , in dry diethyl ether resulted in the replacement of both chloride, Cl^- , ligands with methyl, CH_3 , ligands via transmetalation, a form of ligand exchange reaction between metals that is governed by hard-soft interactions and electronegativities. The formation of the SMe_2 bridged dimeric Pt complex: $[\text{Pt}_2\text{Me}_2(\mu\text{-SMe}_2)_2]$ is facilitated by the dissociation of an SMe_2 ligand from each Pt center. This exists in equilibrium as both the dimeric species **(2)**, the *cis* monomeric species: *cis*- $[\text{Pt}_2\text{Me}_2(\mu\text{-SMe}_2)_2]$ **(1)**, and SMe_2 .

^1H NMR data, including chemical shift (δ) and coupling constants (J) are in relative agreement with those reported in literature.^{3,4} Peaks for Pt-Me and Pt-S-Me all gave clearly defined and identifiable satellites, indicating coupling to ^{195}Pt . Hydrogens belonging the

SMe₂ moiety are found most downfield due to its close proximity to S, an electronegative atom, which draws electron density away. The methyl groups directly bound to the Pt center are the most upfield and most shielded. Additionally, NMR results also indicate a mixture of both the monomeric **(1)** and dimeric **(2)** Pt(II) species. However, the dimeric species is the most dominant product as indicated by its more intense peaks. The identity of the monomeric species is confirmed via comparison of experimental *J* values to literature *J* values.^{3,4}

It is important to note that the molar ratio required to form the subsequent cyclometalated species only requires half of the molar amount of Pt in Pt-dimer. Experimental procedures utilized a 1:2 ratio of dimer to ligand for the synthesis of the cyclometalated Pt(II) species. See Experimental section.

2.2 Synthesis and Characterization of Ligands

The ligands studied in this project were modeled after structures found in the 1998 *Organometallic* publication by Baar et al. employing the use of chiral diimine ligands derived from *cis*- or *trans*-diaminocyclohexane.²³ The original ligand design in the study by Baar et al. contained a chiral diimine cyclohexyl backbone with a pendant aromatic ring, benzene, attached to the imine moiety. This particular ligand design has been shown to react with high stereoselectivity.^{18,20,21,22,23} The study herein sought to replicate similar results with iminic thiophene-based ligands. This was accomplished by introducing the chiral cyclohexyl backbone into the ligand structures to afford di-iminic thiophene-derived ligands containing the cyclohexyl backbone with two stereocenters.

Three variations of the chiral diaminocyclohexane were utilized in the ligand synthesis: *R,R-trans*, *racemic-trans*, and *cis*. The ligands studied were produced via condensation reaction of each amine with 3-thiophenecarboxaldehyde in a 1:2 ratio to afford the following Schiff base ligands, respectively: [*R,R-trans*-1,2-(N=C₄H₄S)₂C₆H₁₀] **L3**, [*rac-trans*-1,2-(N=C₄H₄S)₂C₆H₁₀] **L1**, and [*cis*-1,2-(N=C₄H₄S)₂C₆H₁₀] **L4**. The structures of these ligands are given in the table below.

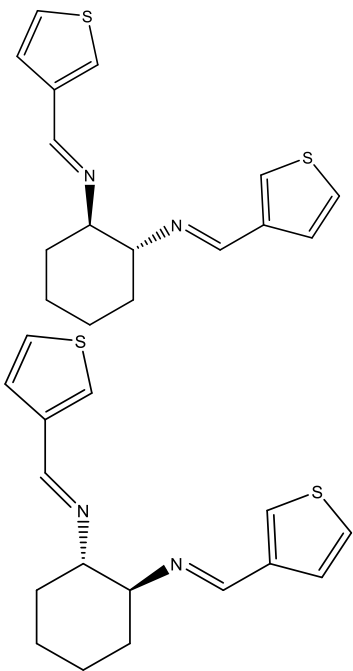
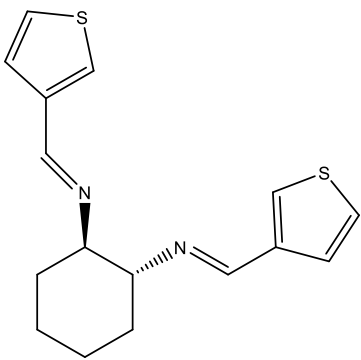
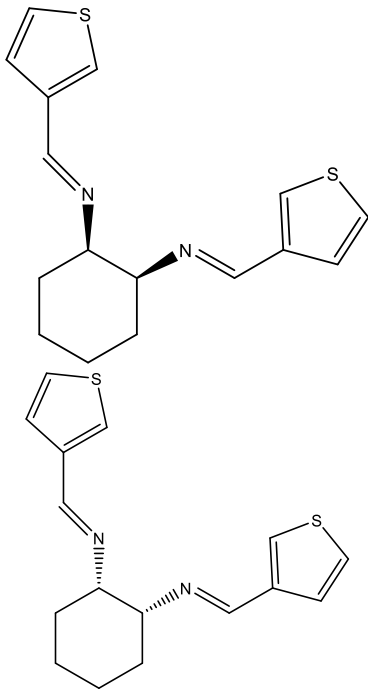
L1	L3	L4
		

Table 2: Ligand Structures

Two important notes must be made. For **L1** and **L4**, there exists two possible ligand structures as they are mixture of enantiomers. **L1** is derived from *racemic-trans*

diaminocyclohexane, which exists as a mixture of both the *R,R* and *S,S* enantiomers in equal amounts. Appropriately, the ligand afforded from this is also a racemic mixture of similar configuration to the parent amine. Similarly, **L4** is derived from *cis*-diaminocyclohexane, which also exists as a mixture of both the *R,S* and *S,R* enantiomers. The Schiff base ligand afforded here is also a mixture of both *R,S* and *S,R* enantiomeric configuration in equal amounts. It is important to note that, ^1H NMR data do not show different resonances for racemic **L1** and **L4** because NMR does not recognize enantiomers. However, it is expected that they do exist. Following synthesis, all ligands were characterized via ^1H -NMR, IR spectroscopy, UV-Visible Spectroscopy, and Emission Spectroscopy. The spectral data for each of these ligands can be found in the Appendices.

L1, **L3**, and **L4** were all successfully synthesized three times following a procedure from an earlier project in 2005.²⁷ The diamine species and thiophene aldehyde were reacted in a 1:2 ratio, with the amine in slight excess and produced a latte-colored powdered solid, in the cases of **L1** and **L3**. Schiff base reaction of **L4**, however, resulted in the formation of a brown oily product, which when left in air, solidified into a latte-brownish colored crystal looking, gummy solid. ^1H -NMR of all these ligands, however, confirm their identities and successful formation. The table below lists important and characteristic ^1H NMR resonances for all the ligands. It is important to note that because these ligands are symmetrical in nature, only single resonances are observed for all the imine C-H peaks (around 8.2 ppm) as they are chemically equivalent. Additionally, the aromatic protons of both thiophene rings only show a set of three peaks, one for each H, indicating that while the individual protons on the rings are chemically inequivalent, both thiophene rings as a whole are equivalent. The chemical inequivalent nature of the

individual protons in the aromatic system stems from the proximity to the S and to the imine moiety. Position 2 on the ring, as it is closest to both the imine moiety and the S, is the peak most downfield due to the electronegative nature of S (which draws electron density away) and its proximity to the imine, which draws additional electron density away as well. Position 5 is the next downfield value due to its close proximity to S, and position 4 is the most upfield of the three protons as it is only proximal to the imine. Moreover, the H on the cyclohexane closest to the N are chemically different than the other cyclohexyl hydrogens.

¹ H NMR Data (400 MHz in CD ₃ COCD ₃) for Ligands				
Complex	δ (ppm)	Multiplicity	Bond Type	# of hydrogens
L1	1.47	m	Cyclohexyl C-H	4
	1.75	m	Cyclohexyl C-H	4
	3.257	m	N-C-H	1
	7.39	d	aromatic	1
	7.47	d	aromatic	1
	7.67	s	aromatic	1
	8.22	s	N=C-H	1
L3	1.477	m	C-H	4
	1.75	m	C-H	4
	3.263	m	N-C-H	1
	7.385	d	aromatic	1
	7.411	d	aromatic	1
	7.649	s	aromatic	1
	8.211	s	N=C-H	1
L4	1.542	m	C-H	4
	1.64	m	C-H	4
	3.4	m	N-C-H	2
	7.439	d	aromatic	1
	7.475	d	aromatic	1
	7.737	s	aromatic	1
	8.292	s	N=C-H	1

Table 3: Characteristic ¹H-NMR resonances for ligands

Additionally, IR data for the ligands were obtained and are found in the Appendix D. Characteristic ν values unique to the ligands were the aromatic C-H stretch of the thiophene ring around 3100 cm^{-1} and the alkyl C-H stretch of the cyclohexyl backbone given by the peaks around $2800\text{--}3000\text{ cm}^{-1}$. Photophysical measurements were also made to characterize the ligands. UV-Visible spectral data can also be found in Appendix B. Results from these measurements show that these ligands do not absorb within the visible spectrum. Peak absorbance wavelengths were found to be around 250 nm (Figure 4).

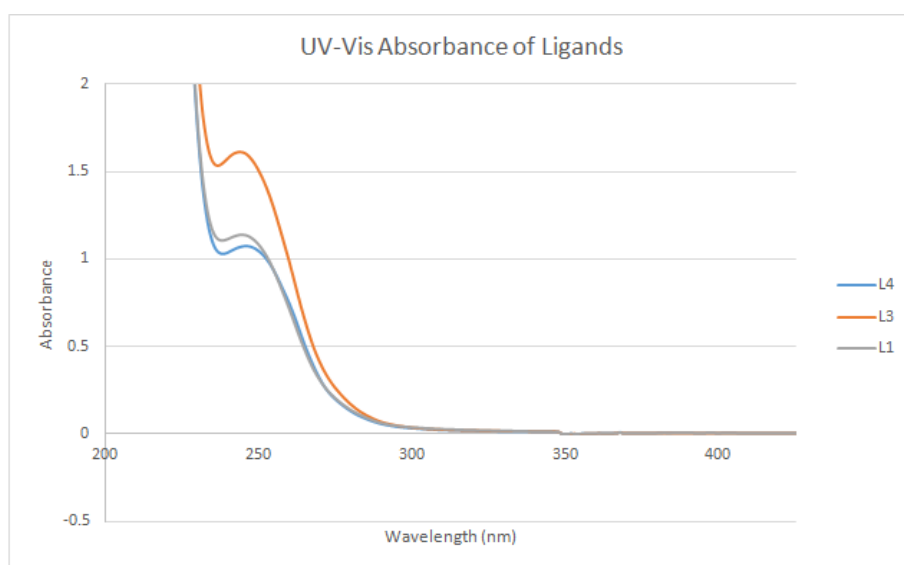


Figure 4: UV-Vis Absorbance of ligands at 0.1 mM concentrations in DCM

However, when excited at these peaks, they show fluorescence emissions around 470 nm. Emission spectra for **L4** is given below (Figure 5) as an example. One important note to make is that sharp peaks can be observed in all emission spectra. These are a result of harmonic overtones of the excitation wavelength. This was confirmed by the fact that these peaks appeared at double the value of the excitation wavelength.

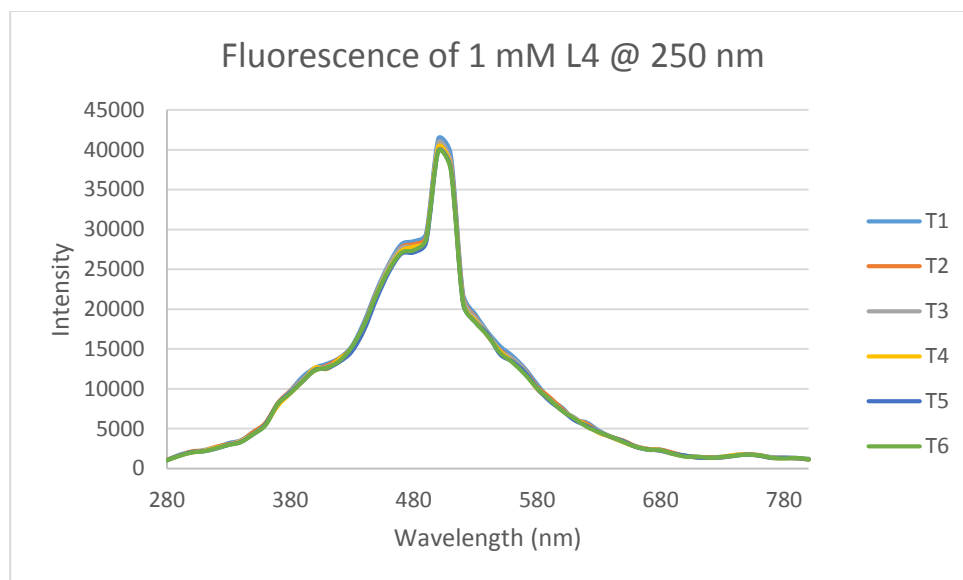


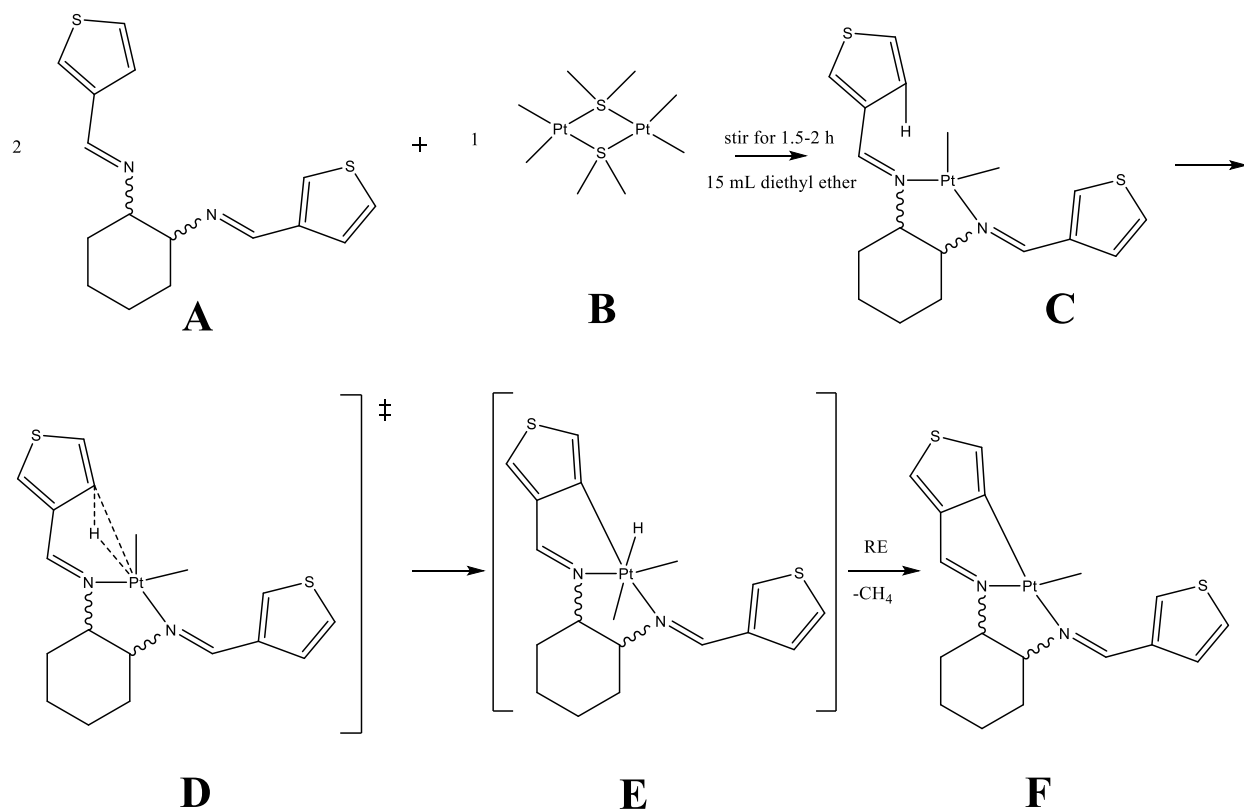
Figure 5: Emission spectra of 1 mM L4 solution in DCM at excitation wavelength of 250 nm. Sharp peak around 500 nm is observed due to harmonic overtones.

Ligand Photophysical Measurements			
	Excitation Wavelength (nm)	Molar Absorptivity ($\text{Lcm} \cdot \text{mol}^{-1}$)	Emission Wavelength (nm)
L1	246	22000	466
L3	247	32000	467
L4	250	22000	470

Table 4: Ligand Photophysical Measurements in DCM.

2.3 Cyclometalation reaction of ligands and $[\text{Pt}_2\text{Me}_2(\mu\text{-SMe}_2)_2]$

The cyclometalation reaction observed in this study is outlined below.



Scheme 1: Cyclometalation of di-iminic thiophene ligands proceeding through an agostically bonded transition state and a transient hydride complex resulting in the formation of a cyclic organometallic product and methane gas.

Pt (II) is introduced to this system as binuclear dimer **B**. However, the stoichiometric relationship of ligand to Pt dimer only requires one Pt atom. Therefore the cyclometalation reaction is carried out in a 2:1 ratio, respectively. The process begins with the coordination of Pt to both N atoms in ligand **A**, representing **L1**, **L3**, and **L4**, via facile dissociation of labile SMe_2 on each Pt center. The initial coordination of Pt to the ligand leads to the formation of κ_2 , or bidentate, chelated Pt (II) complex, **C**. Then as a result of the proximity of the Pt(II) center to the thiophene rings, there exists a potential agostic interaction (shown in **D**) between the $\text{C}_{\text{sp}^2}\text{-H}$ bond of position 2 on the thiophene and the metal center. This interaction, along with the stability engendered by chelation, facilitates the subsequent cyclometalation, as this interaction allows for the sharing of the 2 electrons of

the C_{sp^2} -H with the metal center, creating a pseudo-bond between Pt, position 2 of the ring, and H. Eventually, the C_{sp^2} -H bond is cleaved by intramolecular oxidative addition resulting in the formation of a 5-coordinate Pt(IV) species containing a hydride. This hydride complex, **E**, however, was never observed or isolable. Therefore, this Pt(IV) hydrido complex must in turn be transient and quickly undergoes reductive elimination of the hydride with an adjacent methyl group to form methane gas and the 5 membered, tridentate, *endo*-platinacycle, **F**, $[PtMe\{(N=CHC_4H_5S)-2-(N=CHC_4H_5S)-C_6H_{10}\}]$. The structures of these cyclometalated species are given below.

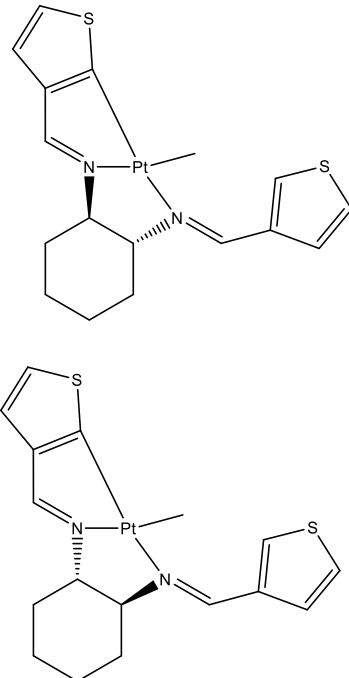
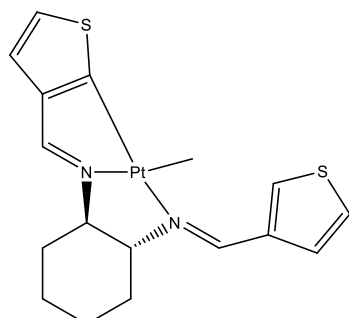
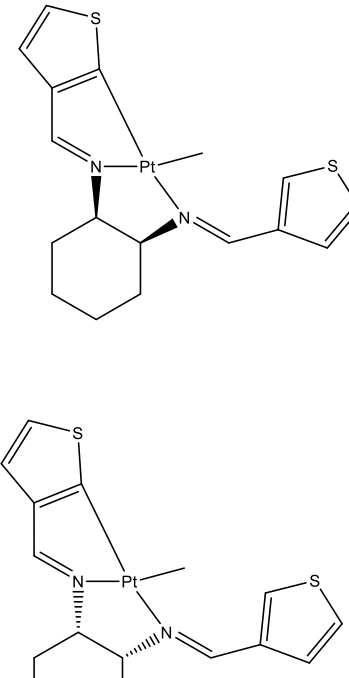
ML1	ML3	ML4
		

Table 5: Structures of the cyclometalated Pt (II) complexes

Two important notes must be made here, as well. As with their parent ligands, the cyclometalated Pt(II) complexes of **L1** and **L4** lend to two possible structures to the final

cyclometalated species as they exist as racemic mixtures. Additionally, it is expected, as suggested by literature, that the oxidative addition step of this reaction is stereoselective, however no conclusive or useful information have been obtained since the intermediate hydride species could not be observed.

ML1 was synthesized was once with great success, while **ML3** and **ML4** were synthesized three times in order to obtain cleaner and better product. **ML1** and initial attempts to synthesize **ML3** and **ML4** were synthesized in accordance to a previous project's procedure²⁷. **ML1**, **ML3** and **ML4** were synthesized successfully in relatively high yields (>85% yield). The two additional trials of **ML3** and **ML4** followed the procedure outlined in the *Organometallic* paper by Baar et al.²³ Similar yields were obtained, however changes to the solvent were made. Instead of the DCM, the reactions were run in diethyl ether, which proved to be useful and helpful for purifying purposes. In diethyl ether, the resulting metalated complexes were insoluble and precipitated at the bottom of the round bottom flask. The insolubility of the compound in diethyl ether made cold ether wash less unfavorable as the compound does not dissolve well, which therefore resulted in the lower amount of product loss during ether wash. All cyclometalation reactions resulted in the yield of a bright red-orange solid.

The cyclometalated Pt (II) complexes were characterized by ¹H-NMR, IR spectroscopy, UV-Visible Spectroscopy, and Fluorescence Spectroscopy. The spectral data for each of these ligands can be found in the Appendices. ¹H-NMR helped to confirm the identities of the above complexes. All chemical shifts, δ , and coupling constants, J , were in close accordance to the Baar et al. paper.²³ Characteristic resonances are given below. All ¹H NMR spectra of metalated ligands contained a single methylplatinum resonance with

coupling constant of $^2J(\text{PtH}) = \sim 83 \text{ Hz}$, which is indicative of platinum's 2+ oxidation state and suggests that the methyl group is *trans* in position to the N donors. Spectra also show characteristic ^{195}Pt satellites on the imine proton resonances with coupling constants of $^3J(\text{PtH})$ around 60 Hz.

^1H NMR Data (400 MHz in CD_3COCD_3) for Pt (II) complexes				
N-Pt-Me			N=CH	
Complex	δ (ppm)	$^2J(\text{PtH})/\text{Hz}$	δ (ppm)	$^3J(\text{PtH})/\text{Hz}$
ML1	0.99	82.4	8.862	62.4
			8.461	56
ML3	0.858	82.8	9.08	63.6
			8.567	58.4
ML4	0.933	82.8	9.148	60
			8.645	59.6

Table 6: ^1H NMR Data (400 MHz in CD_3COCD_3) for Pt (II) complexes with characteristic peaks only being shown.

Additionally, the photophysical properties of the cyclometalated complexes were observed via UV-Visible spectroscopy and emission spectroscopy. Values for peak absorbance and emission wavelength are given in the table below.

Pt (II) Complexes Photophysical Measurements			
	Excitation Wavelength (nm)	Molar Absorptivity ($\text{Lcm}^{-1}\text{mol}^{-1}$)	Emission Wavelength (nm)
ML1	259, 321, 393	21371, 3977, 2510	589, 580, 583
ML3	259, 329, 391	21826, 5565, 3629	599, 589, 591
ML4	265, 332, 400	23473, 6444, 3799	615, 602, 590

Table 7: UV-Vis peak absorption wavelengths and peak emission wavelengths of 0.1 mM solutions of each respective metalated species in DCM.

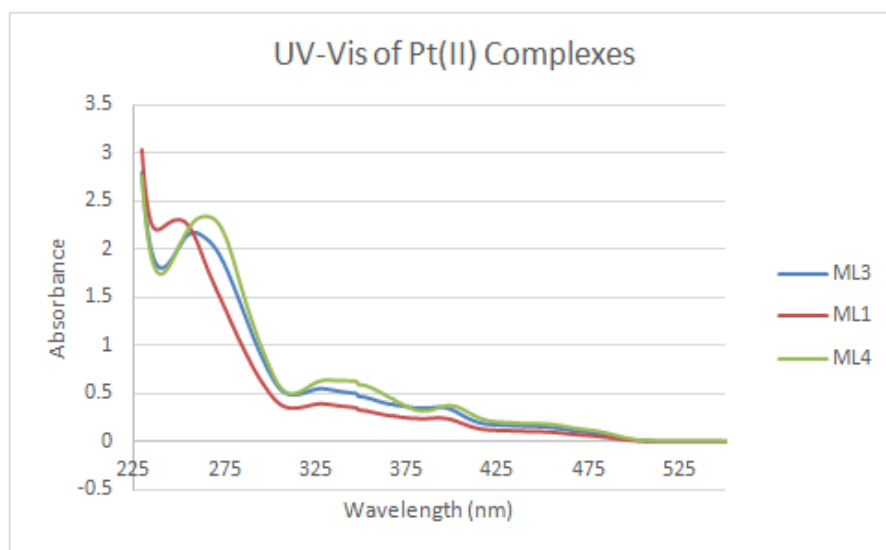


Figure 6: UV-Vis spectral data for cyclometalated Pt (II) complexes in DCM at 10^{-4} concentrations.

The cyclometalated species are shown to have strong absorbances at three different wavelengths (Table 7). The highest energy peaks around 260 nm correspond to ligand absorbances, which have red shifted 12-15 nm from the original ligand absorbance. This is confirmed also by the similar magnitude ($10^4 \text{ Lcm}^{-1}\text{mol}^{-1}$) of the extinction coefficient, ϵ , of the 260 nm metalated peak and 250 nm free ligand peak. This red shift in ligand peak in the Pt(II) species can be attributed to the coordination of ligand to the Pt center, which changes the relative energies of the ligand orbitals. Since the ligands do not absorb in the visible range, the peaks around 330 nm and 400 nm, with molar absorptivities on the order of $10^3 \text{ Lcm}^{-1}\text{mol}^{-1}$, are indicative of metal-ligand charge transfer bands.⁴ When excited at these peak absorbances, peak emission wavelengths fall between 580-615 nm, the red-orange area of the visible spectrum. These fluorescence peaks are expected as the complexes appear in a red-orange color.

2.4 Reaction of [PtMe{(N=CHC₄H₅S)-2-(N=CHC₄H₅S)-C₆H₁₀}] with CH₃I

The stereoselectivity of these complexes was mainly studied through its reaction with methyl iodide. The synthesis of [PtIme₂{(N=CHC₄H₅S)-2-(N=CHC₄H₅S)-C₆H₁₀}] from [PtMe{(N=CHC₄H₅S)-2-(N=CHC₄H₅S)-C₆H₁₀}] and CH₃I followed the procedures given in the 1998 *Organometallics* paper by Baar et al.²³ The aforementioned procedures called for a 1:10 ratio, however initial synthetic attempts for the production of the Pt(IV) species were inconclusive at the 1:10 ratio. ¹H NMR spectral data for initial attempts did not produce any analyzable data. Thus stoichiometric ratios had to be adjusted accordingly. The molar ratio was adjusted to 1:20, which resulted in a better yield of the Pt(IV) product. The resulting products were only characterized via ¹H NMR and IR. Photophysical measurements could not be made because the reaction to produce [PtIme₂{(N=CHC₄H₅S)-2-(N=CHC₄H₅S)-C₆H₁₀}] did not yield pure enough Pt(IV) products. While crude, ¹H NMR data of the oxidative addition products are promising. Close inspection of spectral data shows there are indications of two different products. Characteristic peaks are given in Table 8 below.

	¹ H NMR Data (400 MHz in CD ₃ COCD ₃) for Pt (IV) complexes					
	N-Pt-Me		I-Pt-Me		N=CH	
Complex	δ (ppm)	² J(PtH)/Hz	δ (ppm)	² J(PtH)/Hz	δ (ppm)	³ J(PtH)/Hz
OAL1 (a)	1.098	69.6	0.716	65.6	8.84	-
					8.608	44
(b)	1.108	70.8	0.902	65.6	8.935	-
					8.67	-
OAL3 (a)	1.098	66	.716	69.6	8.840	49.2
					8.607	49.6
(b)	1.287	72.4	.744	70.8	8.884	51.2
					8.649	44
OAL4(a)	1.158	65.6	0.716	69.6	8.973	46
					8.683	48.8
(b)	1.126	70.8	0.744	66	9.002	48.4
					8.702	50

Table 8: ¹H NMR Data for Pt (IV) complexes in CD₃COCD₃. (a) represent values for chemical shift and coupling constant for the major diastereomer formed; (b) represents values for chemical shift and coupling constants for the minor diastereomer.

According to literature, the oxidative addition of methyl iodide from [PtMe{(N=CHC₄H₅S)-2-(N=CHC₄H₅S)-C₆H₁₀}] can result in many isomeric possibilities. However for a given enantiomer of the Pt(II) species, this number is limited to four as a result of the constraints imposed by the tridentate ligand having strong preference for meridional coordination and the Pt(IV) favoring facial coordination of three carbon donor ligands²³. The structures of these isomers are given on the following page.

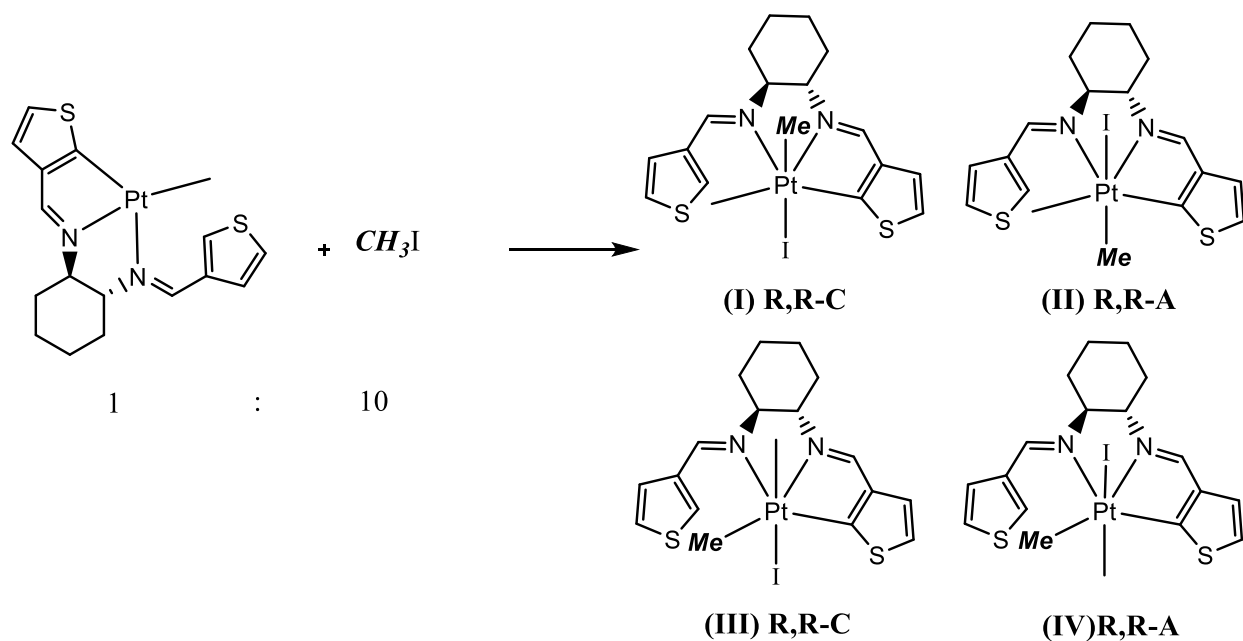


Figure 7: Oxidative addition of methyl iodide to $[R,R\text{-trans-PtI}Me_2\{(N=CHC_4H_5S)-2-(N=CHC_4H_5S)-C_6H_{10}\}]$. The top two structures indicate the isomers resulting from *trans* or S_N2 oxidative addition, while the bottom structures indicate isomers resulting from *cis* addition.

The oxidative addition of methyl iodide (CH_3I or MeI) to the $Pt(II)$ complex can occur through *trans* (or S_N2 type) addition to give **I** and **II** and *cis* (or concerted) addition to give **III** and **IV**. Additionally, for each respective stereochemistry of MeI addition to the $Pt(II)$ species, there two diastereomers possible, as indicated in Figure 6 above as **R,R-C** and **R,R-A**. The labels **C** and **A** define the chirality at the $Pt(IV)$ center since the Me group of MeI can approach and add to either of the two distinct faces of chiral square planar $Pt(II)$ complex during the oxidative addition reaction.²³ Figure 6 above shows the isomeric possibilities for **ML3**. Note, while pure *S,S* enantiomer was not studied, it is expected to yield the similar result as the *R,R* enantiomer: **S,S-C** and **S,S-A**. With the addition of MeI to the $Pt(II)$ compounds, isomers **I** and **III** and **II** and **IV** are structurally equivalent because there is already an existing Me in the coordination sphere. Therefore, there exists only two possible isomers, which is confirmed by NMR data shown below.

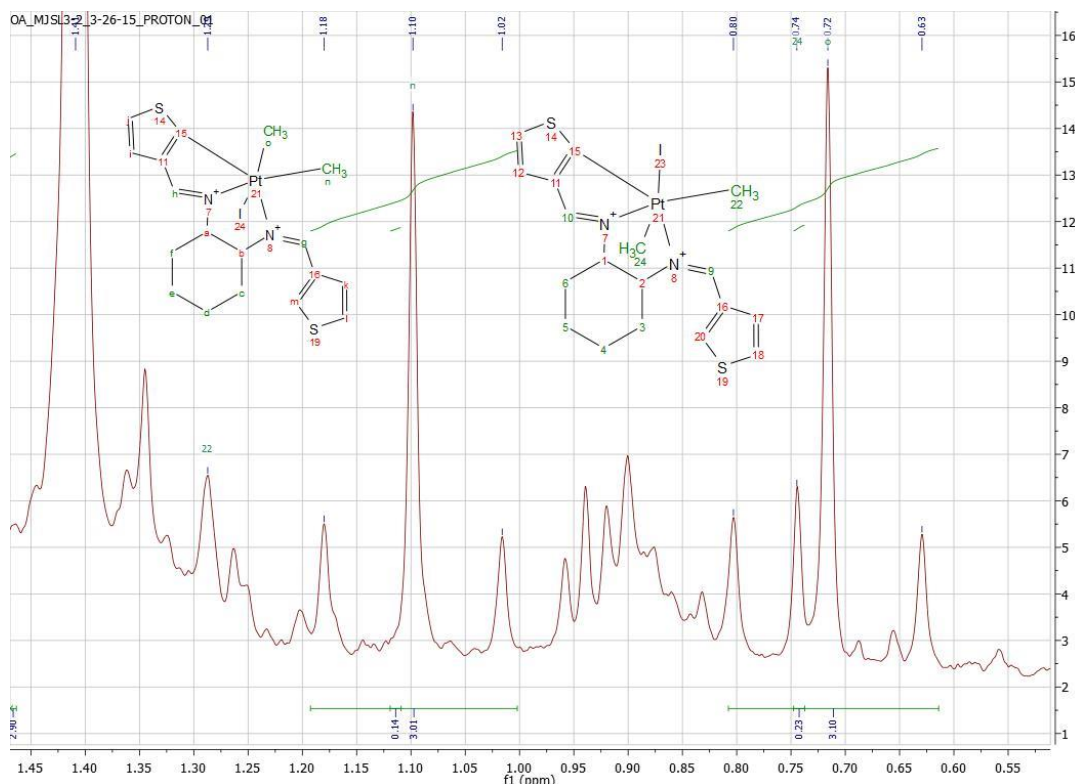


Figure 8: ^1H NMR of OAL3 zoomed in at the Pt-Me resonance region. It is indicative of diastereomeric products. Major diastereomer Pt-Me are labeled as **o** and **n**, while minor diastereomer resonance for Pt-Me are labeled as **22** and **24**.

The major diastereomer formed is posited to be **I**, based on the paper by Baar et al. It has methylplatinum resonances at δ 1.098 with $^2J(\text{PtH}) = 69.6$ Hz and δ 0.716 with $^2J(\text{PtH}) = 65.6$ Hz. The lower frequency resonance is assigned to belong to the methyl *trans* in position to iodide, while the higher frequency is assigned to belong to the methyl group *trans* to the imine moiety. The magnitude of J values are consistent with Pt(IV) species and suggests a *fac*-PtC₃ geometry.²³ Also important to note is that J values were very helpful in structural assignments for other oxidative addition species, as each reaction yielded values within the same range (See Table 8). Additionally, imine protons were present as well with resonances at δ 8.932 with $^3J(\text{PtH}) = 49.2$ Hz and δ 8.604 with $^3J(\text{PtH}) = 49.6$ Hz, indicating that the N donors are still connected to the Pt center. NMR data showed a second set of methylplatinum and imine resonances, indicating the presence of a minor

diastereomer. This was determined to be **II**. Chemical shifts and coupling constants for **II** are reported on Table 8 as (b) for all oxidative addition products. Results for **II** are similar to those obtained for **I**, also suggesting a *fac*-PtC₃ geometry. ¹H NMR data indicates the stereoselectivity of oxidative addition of methyl iodide to [PtMe{(N=CHC₄H₅S)-2-(N=CHC₄H₅S)-C₆H₁₀}] as it shows the major diastereomer having greater resonance than that of the minor diastereomer. Diastereoselective ratio was determined to be 2:1, in favor of **I**.

For *cis*- **ML4**, similar results were obtained, however, the chirality descriptors **C** and **A** are given as *S,R-A* and *S,R-C* and *R,S-C* and *R,S-A* (since **ML4** is racemic). The four possible structures for racemic *cis* are given below.

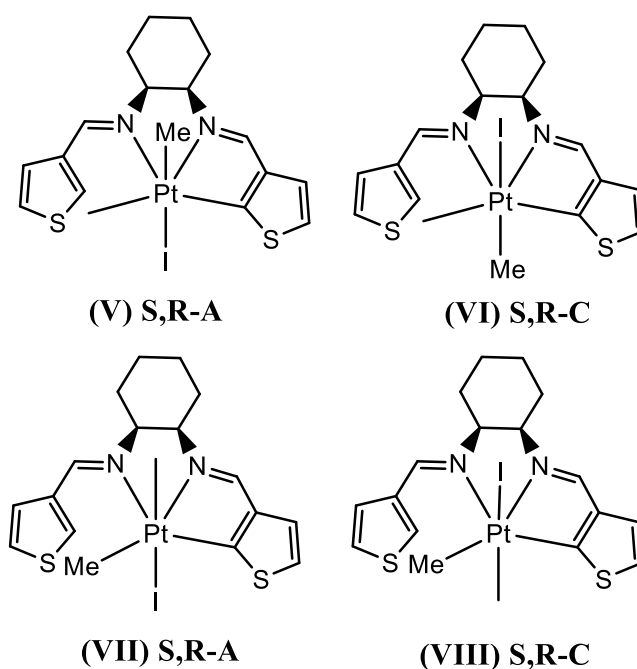


Figure 9: Oxidative addition of MeI to [cis-PtI Me₂{(N=CHC₄H₅S)-2-(N=CHC₄H₅S)-C₆H₁₀}]. The top two structures indicate the isomers resulting from *trans* or S_N2 oxidative addition, while the bottom structures indicate isomers resulting from *cis* addition.

NMR data for the oxidative addition of MeI to [*cis*-PtMe{(N=CHC₄H₅S)-2-(N=CHC₄H₅S)-C₆H₁₀}] is consistent with data from the oxidative addition of MeI on the *trans* complex. Spectral data shows the formation of two diastereomers, with the major diastereomer identified to be **V**. Minor resonances were also observed, however there was overlap of key identifying peaks, making structural assignments very difficult. Diastereoselective ratio was determined to be 2:1, in favor of **V**.

It is expected that the major isomer formed will have the iodide ligand *trans* in position to the cyclohexane ring, which would lie above the plane containing the N[^]N[^]C tridentate ligand, while the methyl group would be *syn* to the cyclohexyl group.²³ The aforementioned is the stereochemistry predicted and possibly expected to be the product of kinetic control as it could minimize the steric effects.²³ Unfortunately, since the respective isomeric possibilities for *trans* and *cis* addition are structurally equivalent, it was not possible to determine whether *trans* or *cis* oxidative addition had occurred. However, since the product generated is *trans* stereochemistry, it is greatly expected that this oxidative addition would most likely go through an S_N2 type mechanism. In theory, this would result in the addition of the methyl group to the least hindered face.²³

3. Concluding Remarks

Multi-dentate thiophene-derived imine ligands, with a cyclohexyl backbone containing a variety of stereocenters were synthesized in high yields (>90% yields). Photophysical measurements indicated that the ligands did not absorb in the visible region, however it was shown to fluoresce around 470 nm, or blue range of the visible spectrum. Its subsequent reactions with Pt dimer resulted in the successful C-H activation of the *ortho* position on only one pendant thiophene. The yields of the cyclometalated species were relatively high (>85% yields). While never directly observed, it is supposed that the intramolecular oxidative addition resulting in the cyclometalated product was stereoselective. The resulting Pt(II) complexes exhibited characteristic bands around 330 nm and 400 nm with molar absorptivity constants on the order of 10^3 magnitude (for molar absorptivity constants see Table 7), which are indicative of ML charge transfer bands. They were shown to fluoresce between 580-615 nm.

Stereoselectivity of these Pt(II) complexes was studied via observing the oxidative addition of CH₃I to each respective Pt(II) complex. No photophysical measurements could be made as the product was crude and ¹H NMR data was not entirely conclusive on the full conversion of Pt(II) to Pt(IV). ¹H NMR data of the resulting oxidative addition species showed traces of Pt(II), indicating the reaction may have not gone entirely to completion. However, ¹H NMR data for all oxidative addition species appeared promising. Close inspection of spectral data reveals the formation of 2 diastereomeric products, with one product dominating. Diastereomeric ratio for both **OAL1**, **OAL3**, and **OAL4** were found to be 2:1, in favor of structures where the adding Me from MeI is syn to the cyclohexyl backbone (Structure **I** of Figure 7 and Structure **V** of Figure 9). However, because the

isomers of both *cis* and *trans* oxidative addition are structurally equivalent, it was not possible to determine the mode of oxidative addition. However, since the product generated has *trans* stereochemistry, it is most likely that *trans* oxidative took place.²³

Further studies regarding the stereoselectivity of these compound could better be elaborated using NMR isotopic studies, as the structural equivalency of the oxidative addition products prevent determination of the mode of oxidative addition. Additionally, instead of MeI, other alkyl halides could be utilized as well. ¹H NMR data was difficult to interpret, largely due to the overlap of several key characteristic peaks. Perhaps cleaner spectra could be obtained by instead observing an intramolecular oxidative addition. Also, for the sake of further understanding the stereoselectivity of these reactions, studies with the S,S variant should also be looked at, as well. When clean and pure products for the Pt(IV) species are made, photophysical measurements should be made for comparison with their respective parent Pt(II) complex.

4. Experimental

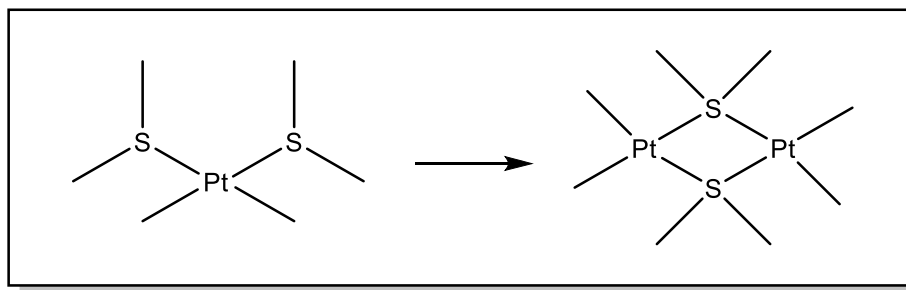
4.1 General

All chemicals utilized in the reaction were purchased from Sigma Aldrich. ^1H NMR spectra were taken at Bard College using a 400 MHz Varian spectrometer in CD_3COCD_3 or CDCl_3 . Residual solvent peaks are identified at 2.08 and 7.26 ppm respectively. Chemical shift, δ , values are given in ppm and all coupling constants, J , values are given in Hz. IR spectroscopy was taken using a Thermo-Nicolet FT-IR Spectrophotometer with a diamond ATR. UV-vis spectra were recorded using Varian Cary 100 UV-Visible Spectrophotometer. Chemical structures were all drawn using CS ChemBioDrawUltra and NMR data was processed using the computer program, MestReNova.

4.2 Photophysical measurements

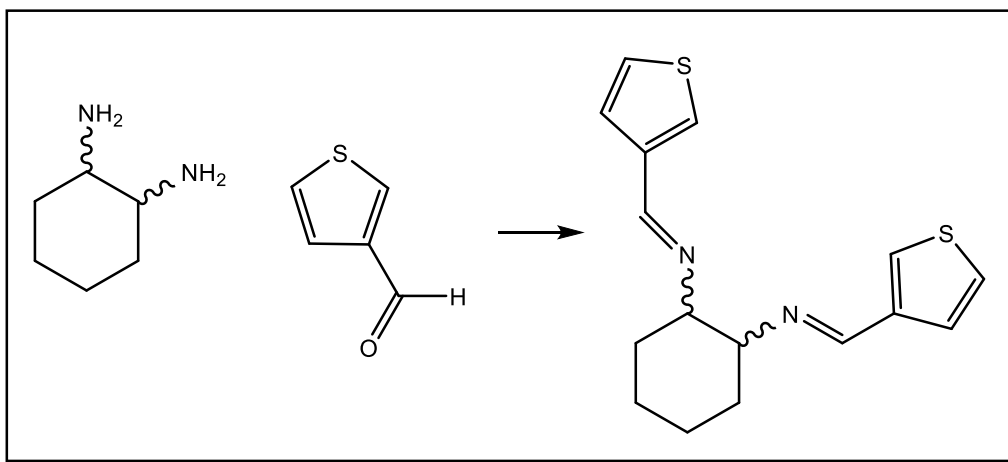
Steady-state emission spectra were recorded using a PTI QM-3 instrument with an R928 PMT detector that is sensitive to 850 nm. The concentration of the solutions for the emission spectra were on the range of 10^{-4} to 10^{-3} M in DCM. Emission spectra were recorded using excitation wavelengths given on Table 4 and Table 7.

4.3 Synthesis of $[\text{Pt}_2\text{Me}_2(\mu\text{-SMe}_2)_2]$



The experimental procedure was carried in dry N_2 atmosphere. In a 100 mL round bottom flask, *cis/trans* dichlorobis(dimethylsulfide) platinum (II) $[\text{PtCl}_2(\text{SMe}_2)_2]$ (0.637 g, 1.82 mmol) was suspended in dry diethylether (40 mL) and purged with N_2 for about 5 minutes. The flask placed in an ice bath for 20 minutes. During that time, methyllithium, MeLi, (7.5 mL, 1.4 M) was added dropwise to the solution via syringe pump. The reaction was stirred for 20 minutes. Additional MeLi (~1 mL) was added after 20 minutes to fully react all the yellow solid in the flask. Once the reaction was finished, when the solution was no longer yellow in color, and instead white, cold, saturated, aqueous NH_4Cl solution (7.5 mL) was added to the white suspension via syringe pump. Cold, distilled H_2O (20 mL) was added very slowly. This resulting solution was then extracted with cold diethyl ether (3x20 mL) and dried with MgSO_4 . The solution was then filtered into a tared round bottom flask. The solvent was then evaporated using the rotary evaporator and dried under high vacuum leaving an off-whitish solid (0.877 g, 83.9% yield). ^1H NMR (400 MHz, CDCl_3): δ = 0.598 [s, 2J = 85.6 Hz, 6H, Me-Pt]; 2.764 [s, 3J = 19.6 Hz, 6H, Me-S-Pt].

4.4 Synthesis of Ligands (L1, L3, L4)



Synthesis of racemic, *trans*-1,2-(N=CHC₄H₃S)₂C₆H₁₀, L1

1st attempt: In a 50 mL round bottom flask, *trans*-1,2 diaminocyclohexane (0.27 mL, 2.25 mmol) and 3-thiophenecarboxaldehyde (0.39 mL, 4.45 mmol) were dissolved in DCM (5 mL). The resulting milky yellow solution was stirred for 1.5 h. Excess MgSO₄ was added to the reaction to remove water produced in the reaction. The solution was filtered into a tared empty round bottom flask and the solvent was removed using the rotary evaporator. The residue formed was washed with hexane and dried under high vacuum for 15 minutes to afford a latte colored powder (0.6425 g, 95.47% yield). ¹H NMR (400 MHz, CD₃COCD₃): δ = 1.47 [m, 2H, Cy(H)], 1.75 [m, 6H, Cy(H)], 3.268 [m, 2H, Cy(H)], 7.385 [m, 1H, aromatic H], 7.426 [m, 1H, aromatic H], 7.667 [d, 1H, aromatic H], 8.217 [s, 1H, N=CH]. FTIR (cm⁻¹) 3107.12, 2922.71, 2660.06, 1637, 1522.25.

2nd attempt: Used 0.3 mL of *trans*-1,2 diaminocyclohexane and 0.4 mL 3-thiophene carboxaldehyde. Stirred for 2 hours.

3rd attempt: Reaction was run in 5 mL acetone

Synthesis of *R,R-trans*-1,2 -(N=CHC₄H₃S)₂C₆H₁₀, L3

In a round bottom flask, *R,R-trans*-1,2 diaminocyclohexane (0.2572 g, 2.25 mmol) and 3-thiophenecarboxaldehyde (0.4 mL, 4.47 mmol) were dissolved in DCM (5 mL). The resulting brownish solution was stirred for 1.5 hr. Solvent was removed using rotary evaporator. The residue formed was washed with hexane and dried under high vacuum to afford a latte colored powder (0.6594 g, 95.5% yield). ¹H NMR (400 MHz, CD₃COCD₃): δ = 1.486 [m, 2H, Cy(H)], 1.75 [m, 6H, Cy(H)], 3.243 [m, 2H, Cy(H)], 7.385 [m, 1H, aromatic H], 7.414 [m, 1H, aromatic H], 7.649 [d, 1H, aromatic H], 8.211 [s, 1H, N=CH]. FTIR (cm⁻¹) 3086.13, 3059.11, 2926.99, 2852.59, 2852.49, 1637.53, 1520.06.

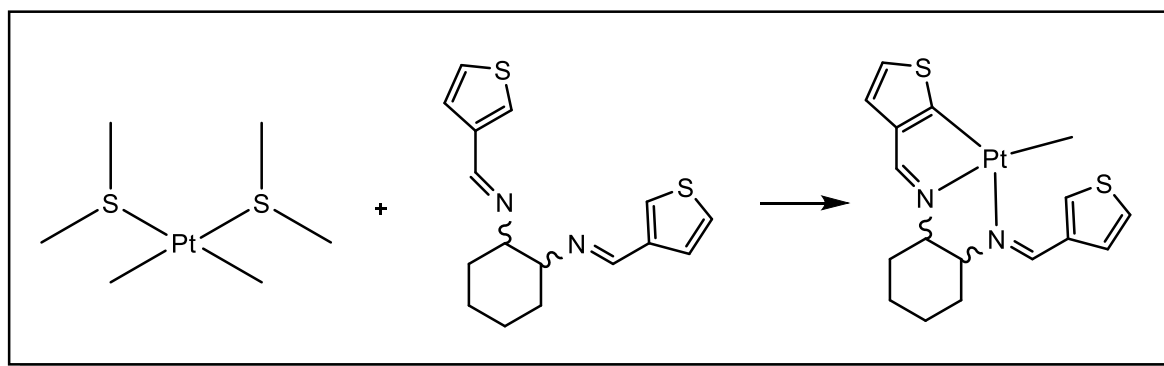
Synthesis of *cis*-1,2 -(N=CHC₄H₃S)₂C₆H₁₀, L4

1st attempt: In a round bottom flask, *cis*-1,2 diaminocyclohexane (0.32 mL, 2.67 mmol) and 3-thiophenecarboxaldehyde (0.4 mL, 4.47 mmol) were dissolved in DCM (5 mL). The resulting brownish solution was stirred for 1.5 hr. Solvent was removed using rotary evaporator. The residue formed was washed with hexane and dried under high vacuum to afford a milky brown, gummy solid (0.6594 g, 95.5% yield). ¹H NMR (400 MHz, CD₃COCD₃): δ = 1.542 [m, 2H, Cy(H)], 1.640 [m, 6H, Cy(H)], 3.402 [m, 2H, Cy(H)], 7.439 [m, 1H, aromatic H], 7.475 [m, 1H, aromatic H], 7.737 [d, 1H, aromatic H], 8.292 [s, 1H, N=CH]. FTIR (cm⁻¹) 3075.85, 3073.33, 2930.90, 2848.19, 1630.19, 1524.04.

2nd attempt: Ran the reaction in diethyl ether (8 mL) and added excess MgSO₄. After 1.5 h, the solution was filtered into a tared round bottom flask. The solvent was removed using the rotary evaporator and dried under high vacuum.

3rd attempt: Ran reaction in same way as the second attempt, but let it stir for 48h.

4.5 Synthesis of Cyclometalated Pt (II) Species (ML1, ML2, ML4):



Synthesis of racemic [*trans*-PtMe{(N=CHC₄H₅S)-2-(N=CHC₄H₅S)-C₆H₁₀}], ML1:

In a round bottom flask, **L1** (0.2576 g, 0.852 mmol) and Pt-dimer (0.2367 g, 0.412 mmol) were dissolved in DCM (25 mL). A color change from yellow-orange to red-orange was observed. The resulting solution was stirred for 1.5h. Solvent was removed using rotary evaporator. The residue formed was washed carefully with cold diethyl ether (5-10 mL) and dried under high vacuum to afford a red-orange solid (0.1783 g, 84.6% yield). ¹H NMR (400 MHz, CD₃COCD₃): δ = 0.986 [s, 3H, ²J(PtH)= 82.4 Hz ,Pt-CH₃], 8.457 [s, 1H, ³J(PtH)= 56 Hz ,H-C=N], 8.862 [s, 1H, ³J(PtH)= 62.4 Hz, H-C=N]. FTIR (cm⁻¹) 3084.67, 3063.09, 2923.17, 2786.13, 2848.55, 2796.36, 1637.02, 1586.42.

Synthesis of [*R,R-trans*-PtMe{(N=CHC₄H₅S)-2-(N=CHC₄H₅S)-C₆H₁₀}], ML3:

Attempt 1: In a round bottom flask, **L3** (0.0409 g, 0.135 mmol) and Pt-dimer (0.0206 g, 0.359 mmol) were dissolved in DCM (~20 mL). A color change from yellow-orange to red-orange was observed. The resulting solution was stirred for 1.5h. Solvent was removed using rotary evaporator. The residue formed was washed carefully with cold diethyl ether (5-10 mL) and dried under high vacuum to afford a red-orange solid (0.066 g, 95.5% yield). ¹H NMR (400 MHz, CD₃COCD₃): δ = 0.858 [s, 3H, ²J(PtH)= 82.8 Hz, Pt-CH₃], 1.5-2.0 [m, 8H, Cy(H)], 4.0-5.0 [m, 2H, Cy(H)-N], 7.0-8.0 [d, 3H, aromatic H], 8.567 [s, 1H, ³J(PtH)= 58.4 Hz, H-C=N], 9.08 [s, 1H, ³J(PtH)= 63.6 Hz, H-C=N]. FTIR (cm⁻¹) 3113.41, 2921.91, 2854.59, 2798.24, 1619.03, 1581.33, 1527.24.

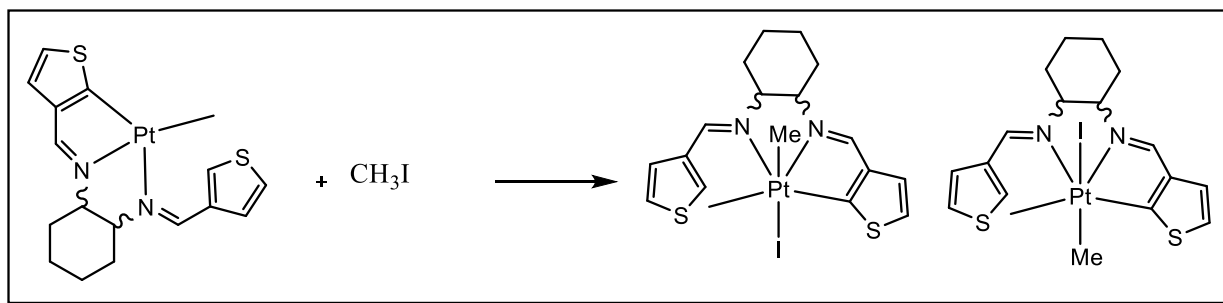
Attempt 2: Ran reaction in diethyl ether (20 mL).

Synthesis of [*cis*-PtMe{(N=CHC₄H₅S)-2-(N=CHC₄H₅S)-C₆H₁₀}], ML4:

Attempt 1: In a round bottom flask, **L4** (0.0290 g, 0.959 mmol) and Pt-dimer (0.0275 g, 0.479 mmol) were dissolved in acetone (~12 mL). A color change from yellow-orange to red-orange was observed. The resulting solution was stirred for 1.5h. Solvent was removed using rotary evaporator. The residue formed was washed carefully with cold diethyl ether (5-10 mL) and dried under high vacuum to afford a red-orange solid (0.0487 g, 99.4% yield). ¹H NMR (400 MHz, CD₃COCD₃): δ = 0.933 [s, 3H, ²J(PtH)= 82.8 Hz, Pt-CH₃], 1.5-2.0 [m, 8H, Cy(H)], 4.0-5.0 [m, 2H, Cy(H)-N], 7.0-8.0 [d, 3H, aromatic H], 8.645 [s, 1H, ³J(PtH)= 59.6 Hz, H-C=N], 9.08 [s, 1H, ³J(PtH)= 60 Hz, H-C=N]. FTIR (cm⁻¹) 3112.91, 3085.35, 2924.29, 2854.33, 2797.63, 1616.91, 1580.94, 1526.78.

Attempt 2: Ran reaction in diethyl ether (20 mL).

4.6 Oxidative Addition of Methyl Iodide to Cyclometalated Pt (II) Species (OAL1, OAL2, OAL4)



Synthesis of racemic [*trans*-PtI₂Me₂{(N=CHC₄H₅S)-2-(N=CHC₄H₅S)-C₆H₁₀}], OAL1:

In a round bottom flask, **ML1** (0.0161 g, 0.315 mmol) was dissolved in THF (20 mL). Methyl iodide (0.045 mL, ~10 mol) was added to the resulting reddish solution. A color change from red-orange to pale yellow was observed after an hour of reaction. The reaction mixture was stirred for 1.5 h after which the solvent was removed via rotary evaporator and the resulting residue was carefully washed with acetone (5-10 mL) and dried under high vacuum to afford a yellow solid. No accurate yield could be obtained. δ = 0.716 [s, 3H, $^2J(\text{PtH})$ = 65.6 Hz, I-Pt-Me], 0.902 [s, 3H, $^2J(\text{PtH})$ = 65. Hz, I-Pt-Me], 1.098 [s, 3H, $^2J(\text{PtH})$ = 69.6 Hz, N-Pt-Me], 1.108 [s, 3H, $^2J(\text{PtH})$ = 70.8 Hz, I-Pt-Me], 1.5-2.0 [m, 8H, Cy(H)], 4.0-5.0 [m, 2H, Cy(H)-N], 7.0-8.0 [d, 3H, aromatic H], 8.608 [s, 1H, $^3J(\text{PtH})$ = 44 Hz, H-C=N], 8.67 [s, 1H, $^3J(\text{PtH})$ = n/a, H-C=N], 8.84 [s, 1H, $^3J(\text{PtH})$ = n/a, H-C=N]. 8.935 [s, 1H, $^3J(\text{PtH})$ = n/a H-C=N]. FTIR (cm⁻¹) 3113.45, 3085.43, 2924.23, 2855.52, 2801.75, 1620.04, 1586.80, 1527.71.

Synthesis of [*R,R-trans*-PtMe₂{(N=CHC₄H₅S)-2-(N=CHC₄H₅S)-C₆H₁₀}], OAL1:

1st attempt: In a round bottom flask, **ML3** (0.0134 g, 0.262 mmol) was dissolved in THF (20 mL). Methyl iodide (0.02 mL, ~10 mol) was added to the resulting reddish solution. A color change from red-orange to pale yellow was observed after an hour of reaction. The reaction mixture was stirred for 1.5 h after which the solvent was removed via rotary evaporator and the resulting residue was carefully washed carefully with diethyl ether (5-10 mL) and dried under high vacuum to afford a yellow solid (0.0161, 94.1%). δ = 0.716 [s, 3H, 2J (PtH) = 69.6 Hz, I-Pt-Me], 0.744 [s, 3H, 2J (PtH) = 70.8 Hz, I-Pt-Me], 1.098 [s, 3H, 2J (PtH) = 65.6 Hz, N-Pt-Me], 0.9 [s, 3H, 2J (PtH) = 62 Hz, I-Pt-Me], 1.5-2.0 [m, 8H, Cy(H)], 4.0-5.0 [m, 2H, Cy(H)-N], 7.0-8.0 [d, 3H, aromatic H], 8.604 [s, 1H, 3J (PtH) = 49.6 Hz, H-C=N], 8.667 [s, 1H, 3J (PtH) = 44 Hz, H-C=N], 8.932 [s, 1H, 3J (PtH) = 49.2, H-C=N], 8.969 [s, 1H, 3J (PtH) = 51.2, H-C=N]. FTIR (cm⁻¹) 3114.23, 3086.02, 2927.30, 2902.12, 2855.24, 2801.78, 1620.57, 1582.35, 1527.56.

2nd attempt: Stoichiometric ratio of CH₃I to Pt(II) species was increased from 10 mol equivalent to 20 mol equivalent.

Synthesis of racemic [*cis*-PtMe₂{(N=CHC₄H₅S)-2-(N=CHC₄H₅S)-C₆H₁₀}], OAL1:

In a round bottom flask, **ML4** (0.0133 g, 0.260 mmol) was dissolved in THF (20 mL). Methyl iodide (0.035 mL, ~20 mol) was added to the resulting reddish solution. A color change from red-orange to pale yellow was observed after an hour of reaction. The reaction mixture was stirred for 1.5 h after which the solvent was removed via rotary evaporator and the resulting residue was carefully washed carefully with acetone (5-10

mL) and dried under high vacuum to afford a yellow solid (0.0161 g, 94.7%). δ = 0.822 [s, 3H, $^2J(\text{PtH})$ = 73.2 Hz, I-Pt-Me], 0.863 [s, 3H, $^2J(\text{PtH})$ = 73.6 Hz, I-Pt-Me], 1.158 [s, 3H, $^2J(\text{PtH})$ = 65.2 Hz, N-Pt-Me], 1.109 [s, 3H, $^2J(\text{PtH})$ = n/a, I-Pt-Me], 1.5-2.0 [m, 8H, Cy(H)], 4.0-5.0 [m, 2H, Cy(H)-N], 7.0-8.0 [d, 3H, aromatic H] 8.683 [s, 1H, $^3J(\text{PtH})$ = 48.8 Hz, H-C=N], 8.702 [s, 1H, $^3J(\text{PtH})$ = 50 Hz, H-C=N], 8.973 [s, 1H, $^3J(\text{PtH})$ = 46, H-C=N], 9.002 [s, 1H, $^3J(\text{PtH})$ = 48.4, H-C=N]. FTIR (cm^{-1}) 3114.64, 3084.48, 2927.08, 2903.67, 2856.01, 1621.07, 1582.09, 1527.83.

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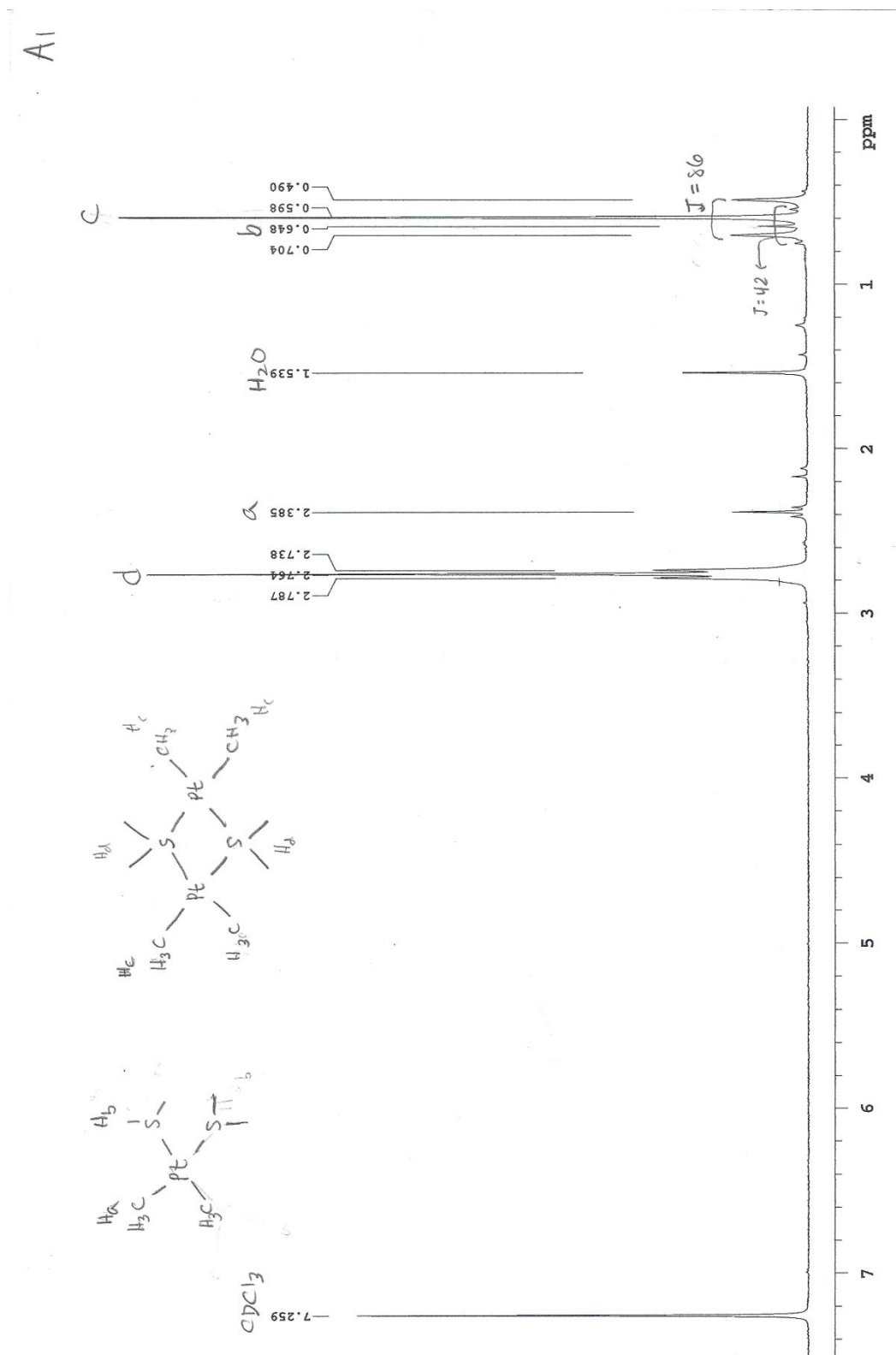
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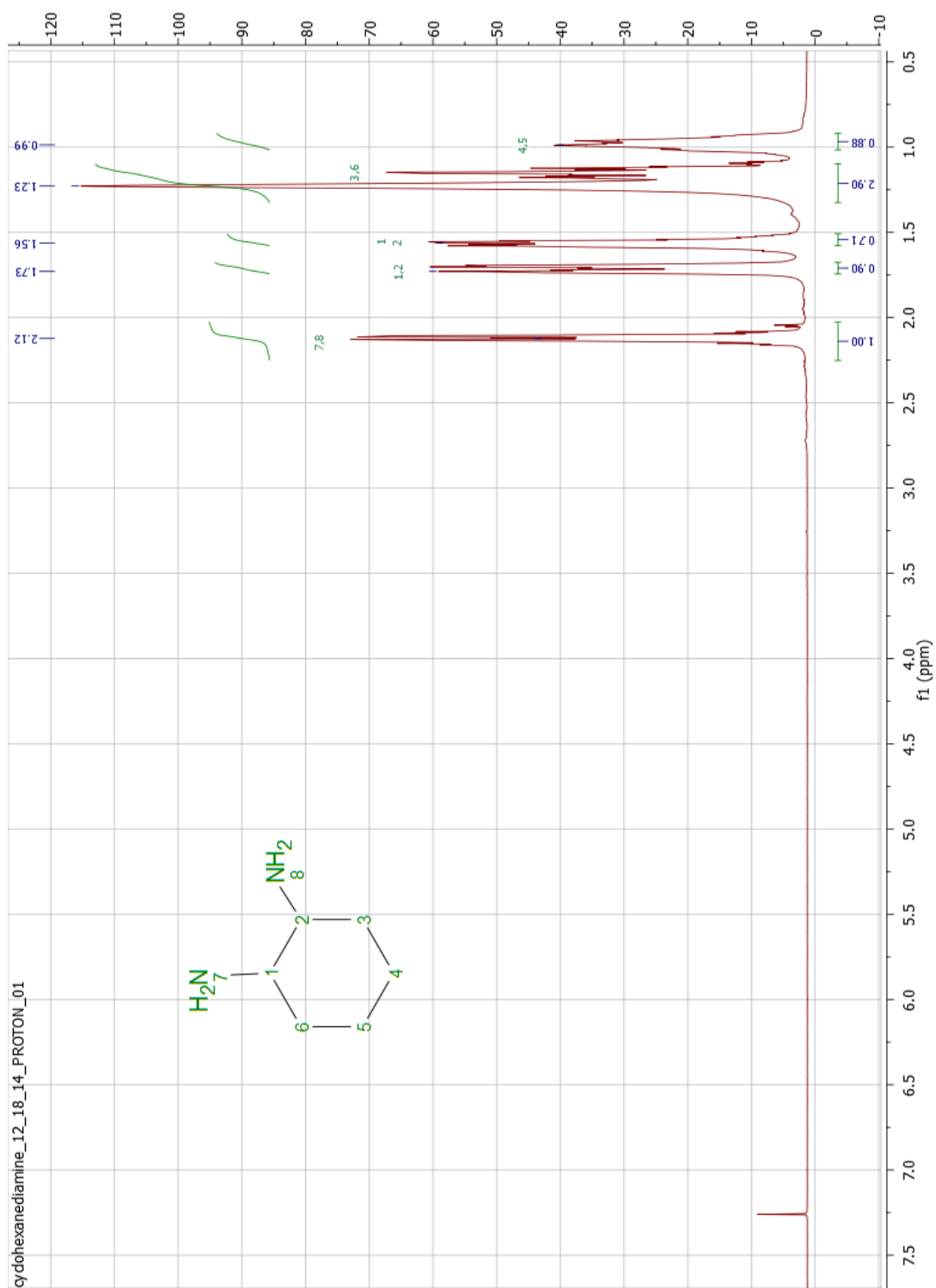
6. References

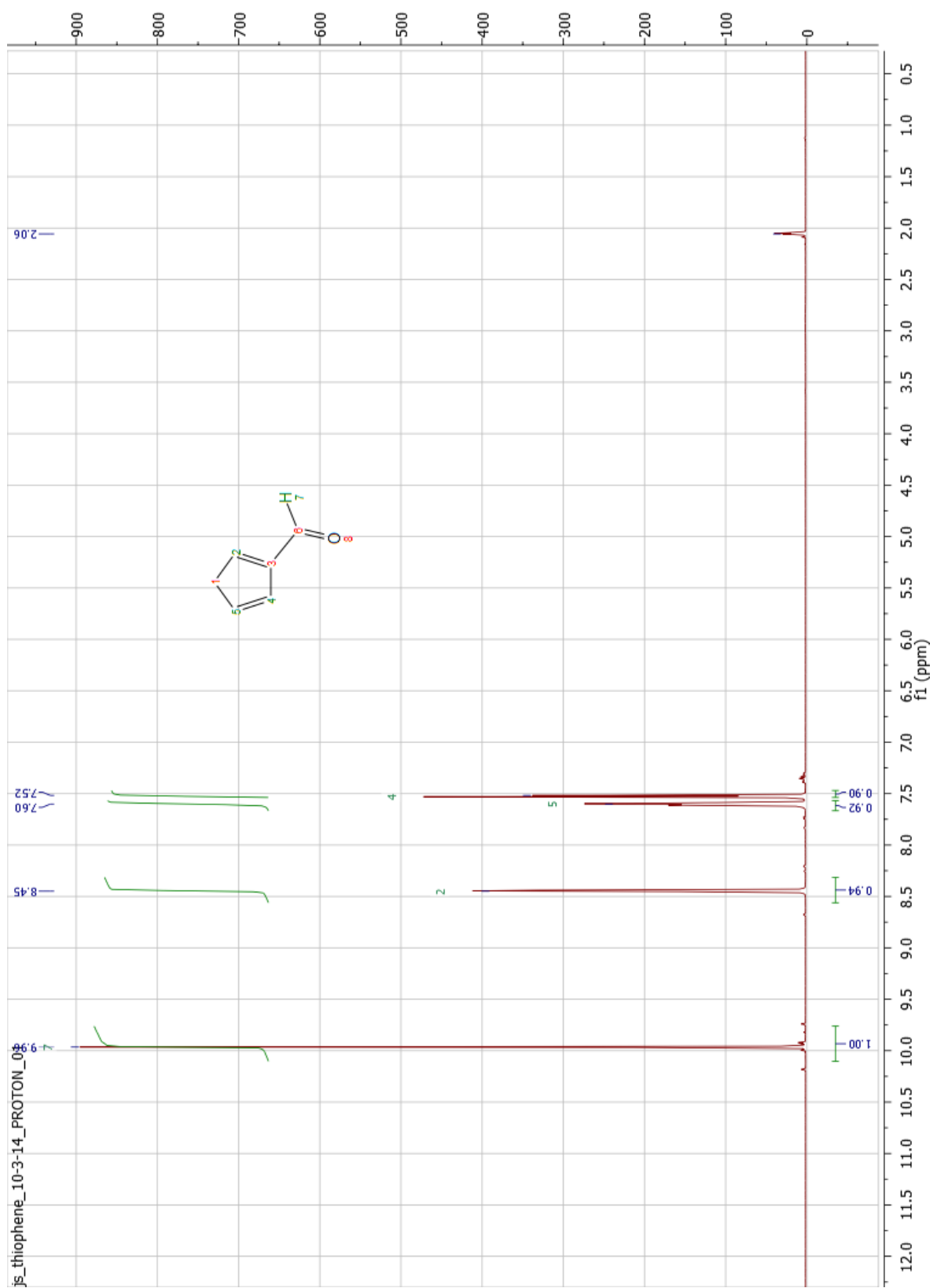
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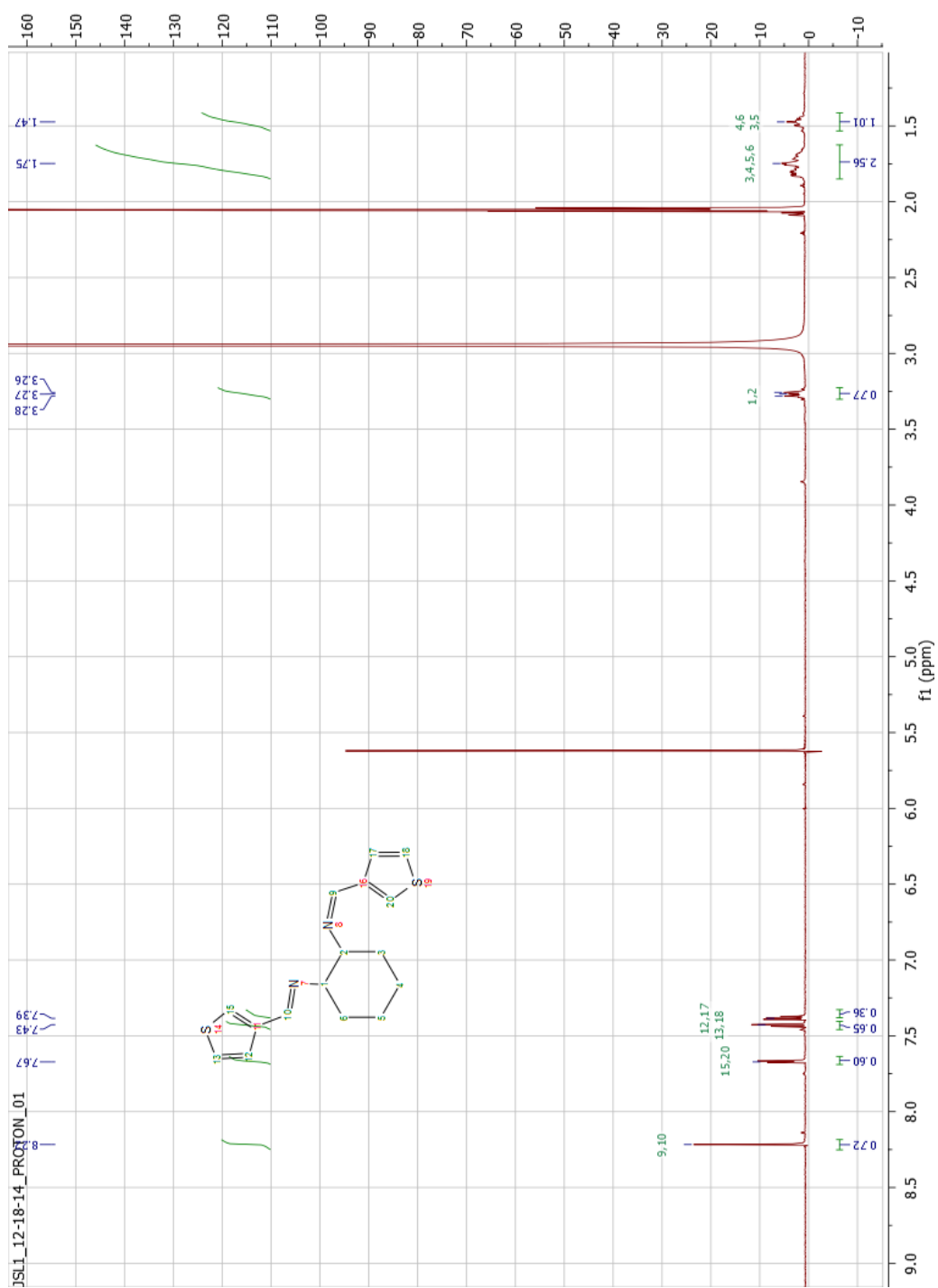
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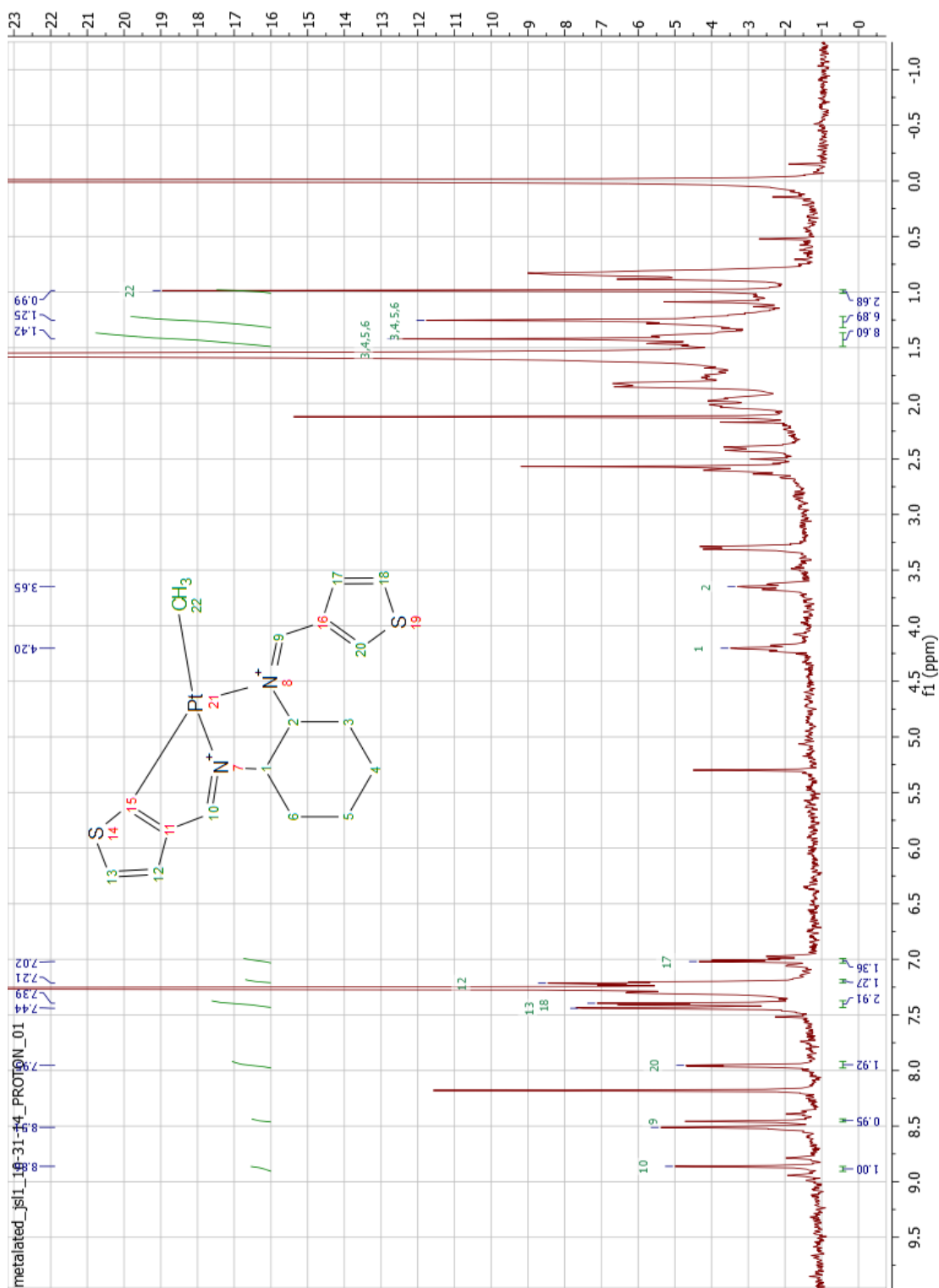
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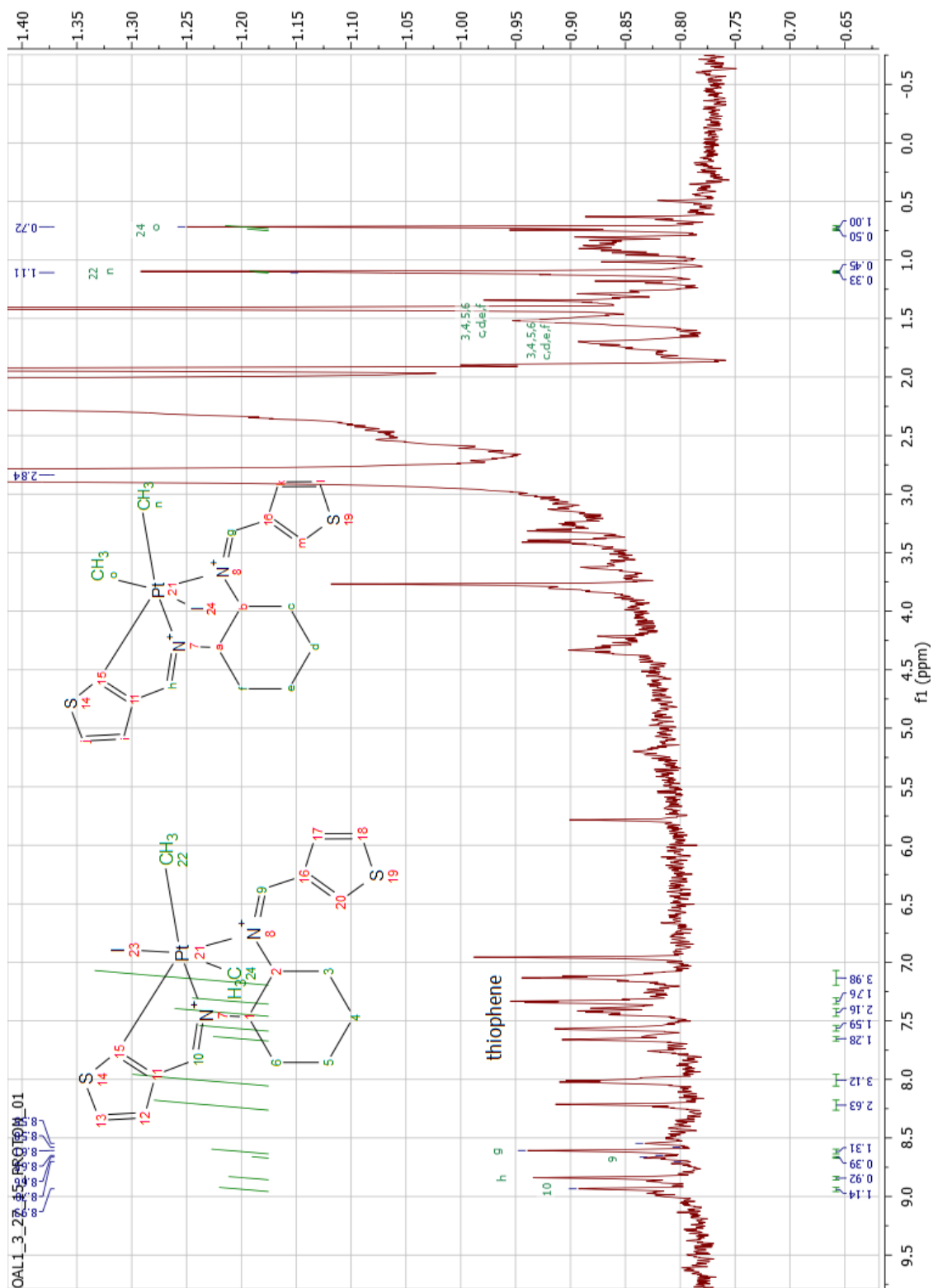
7. Appendix A: ^1H NMR Spectra

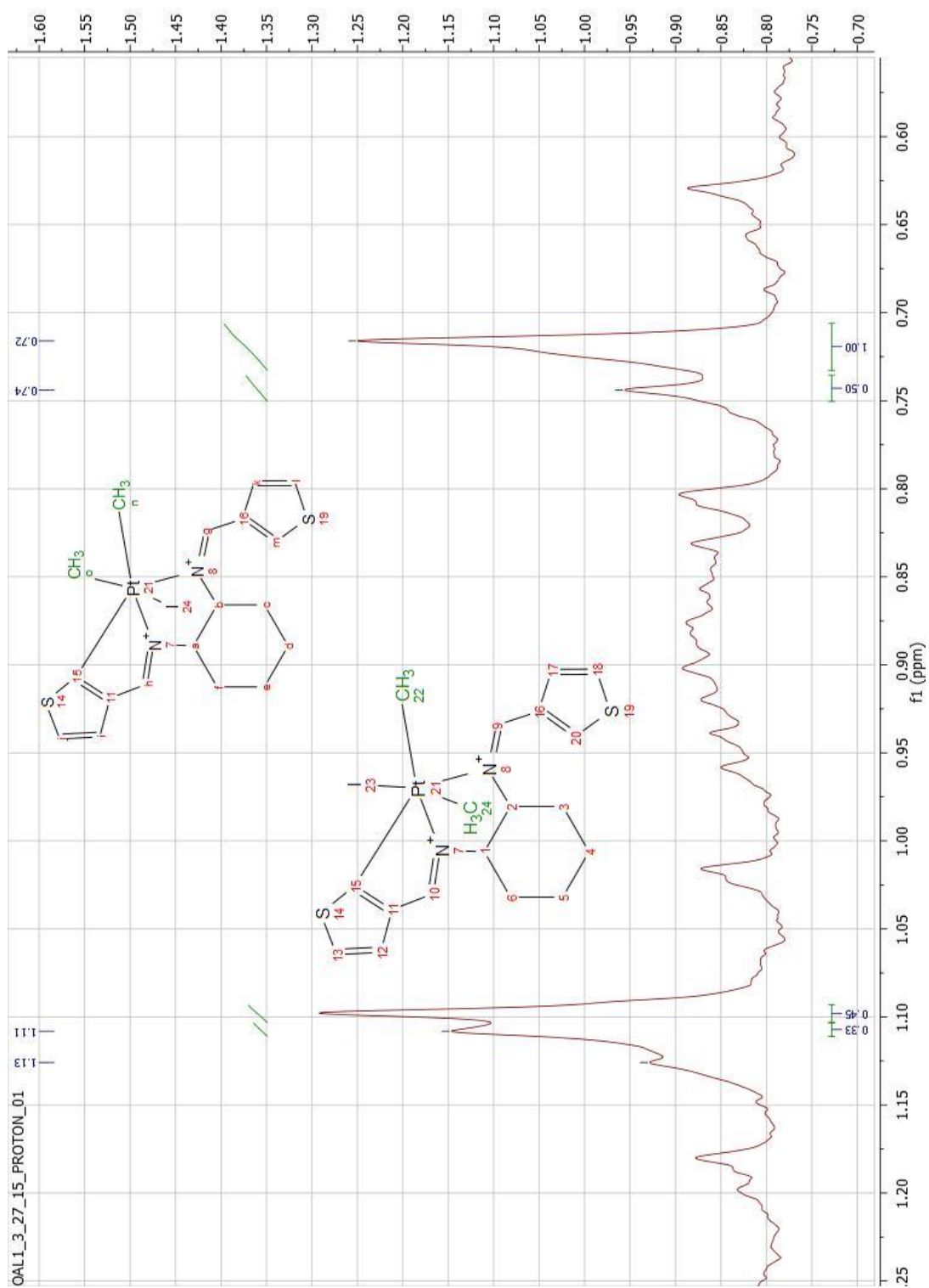


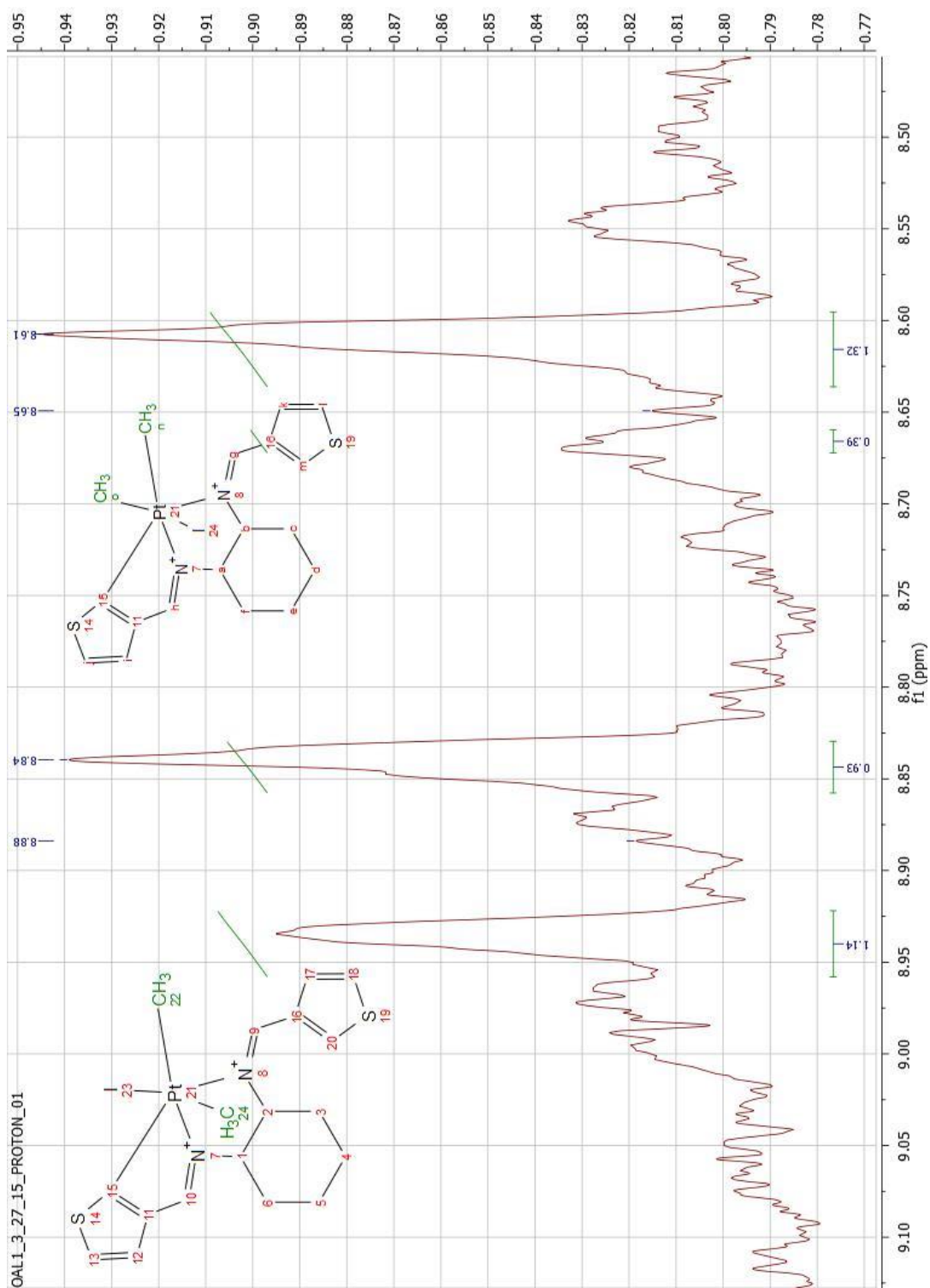


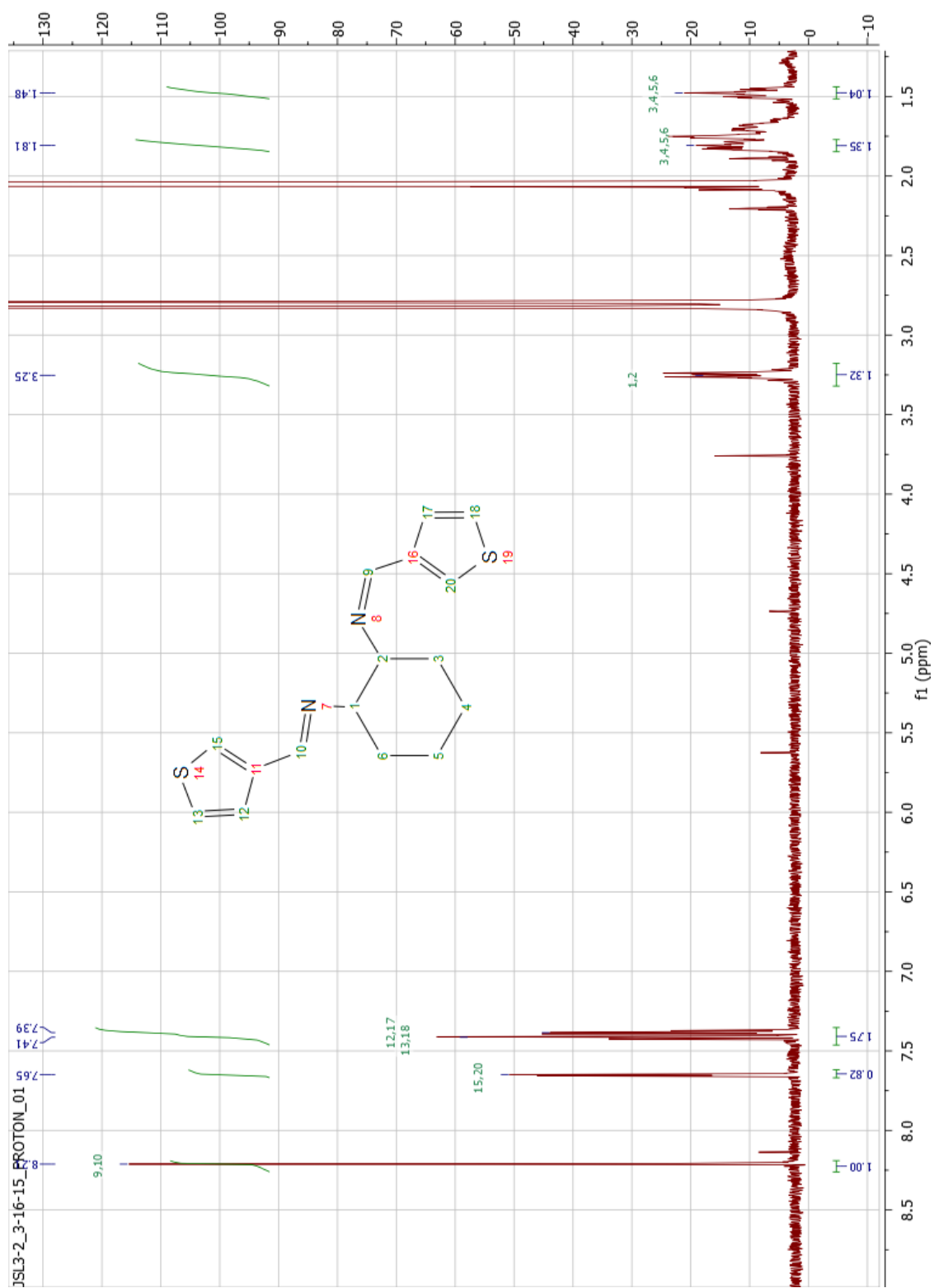


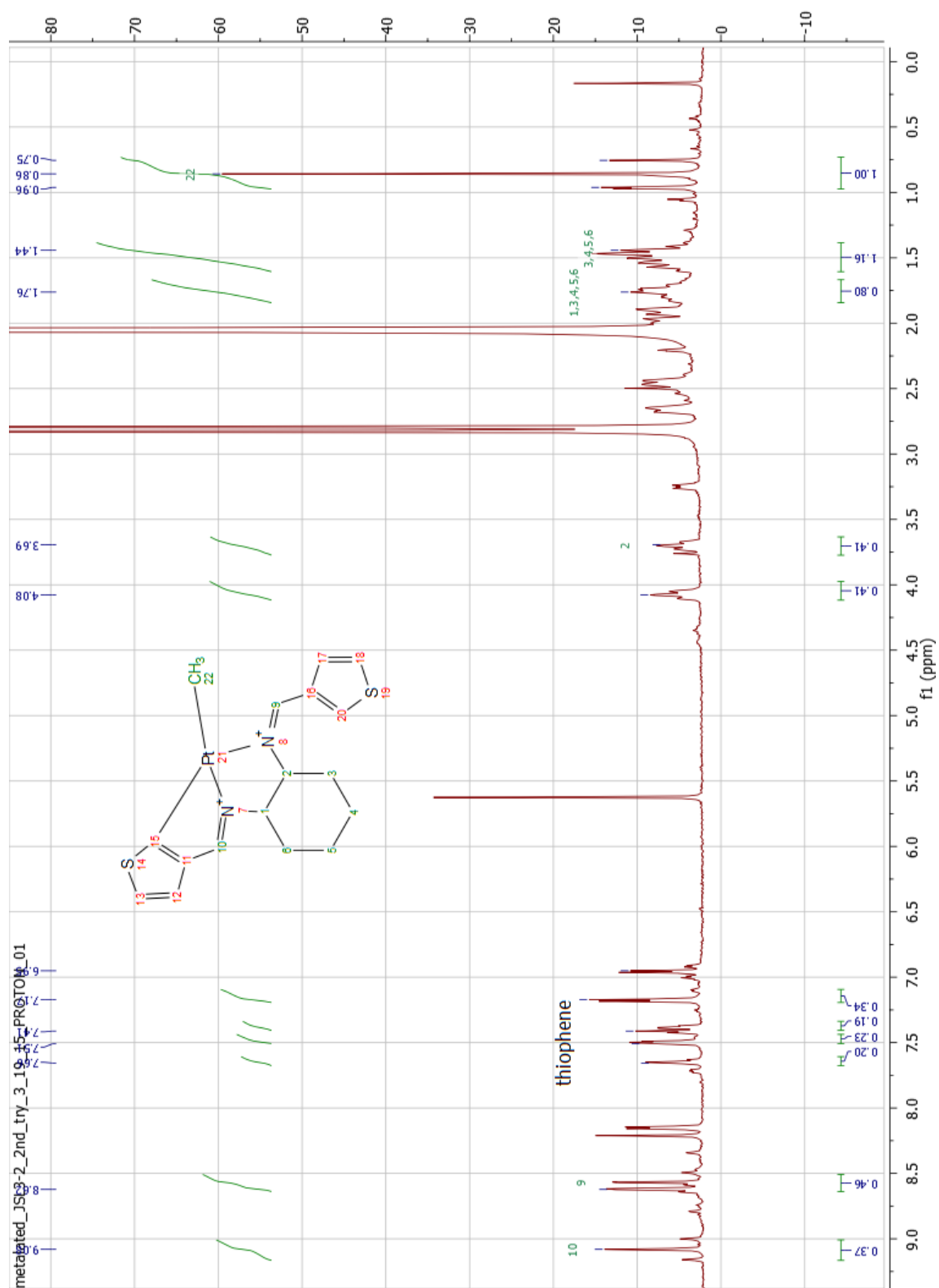


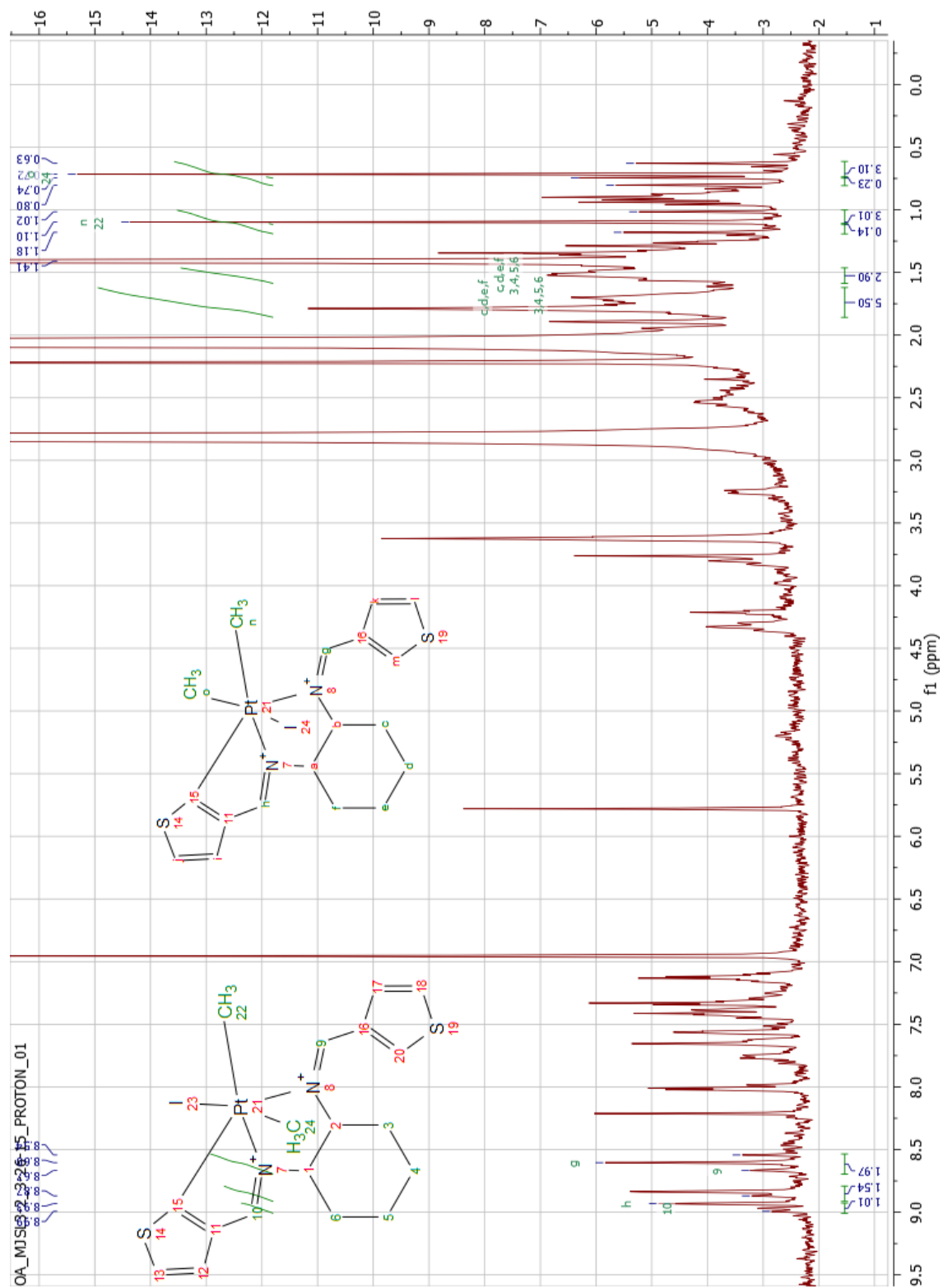


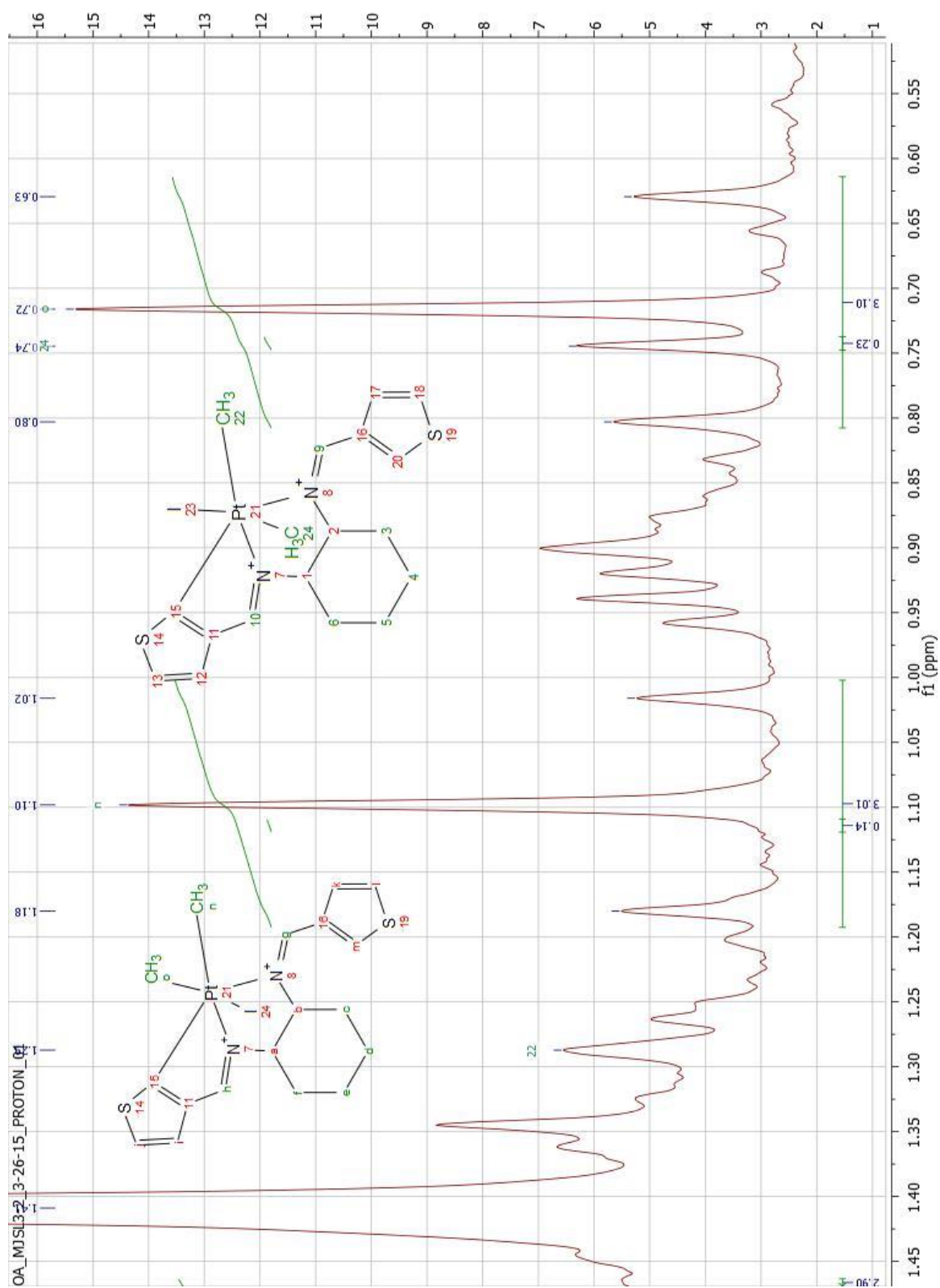


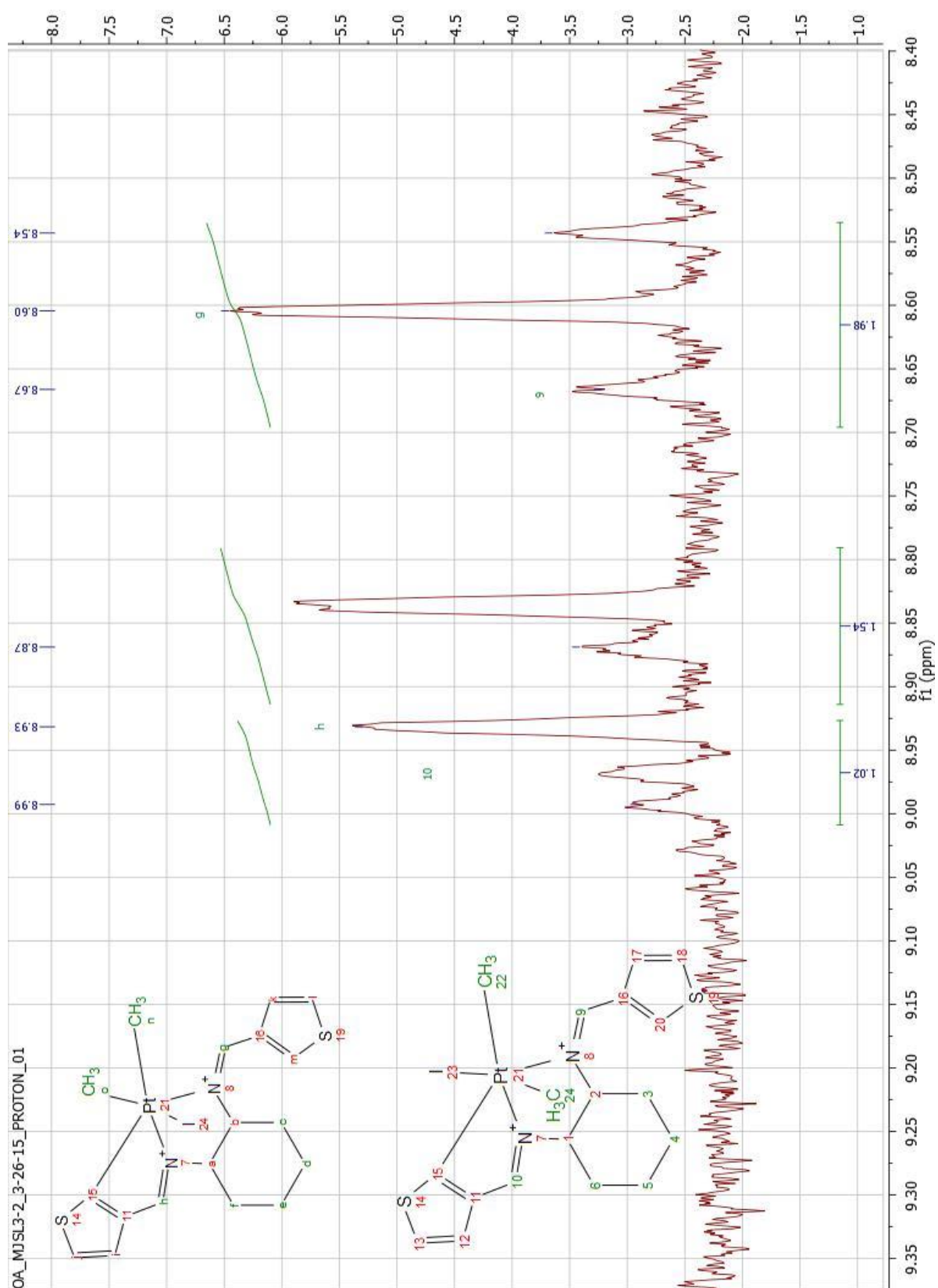


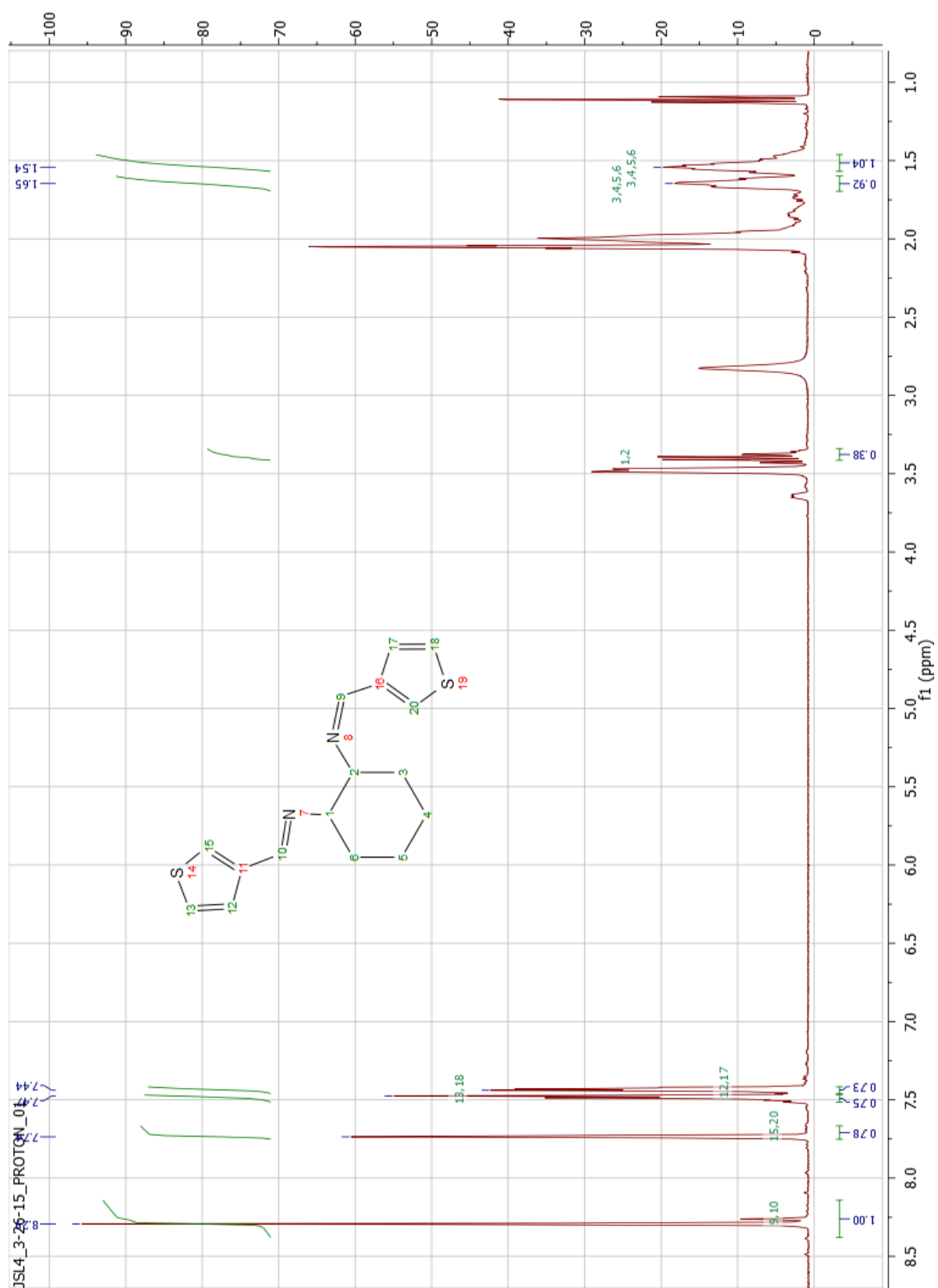


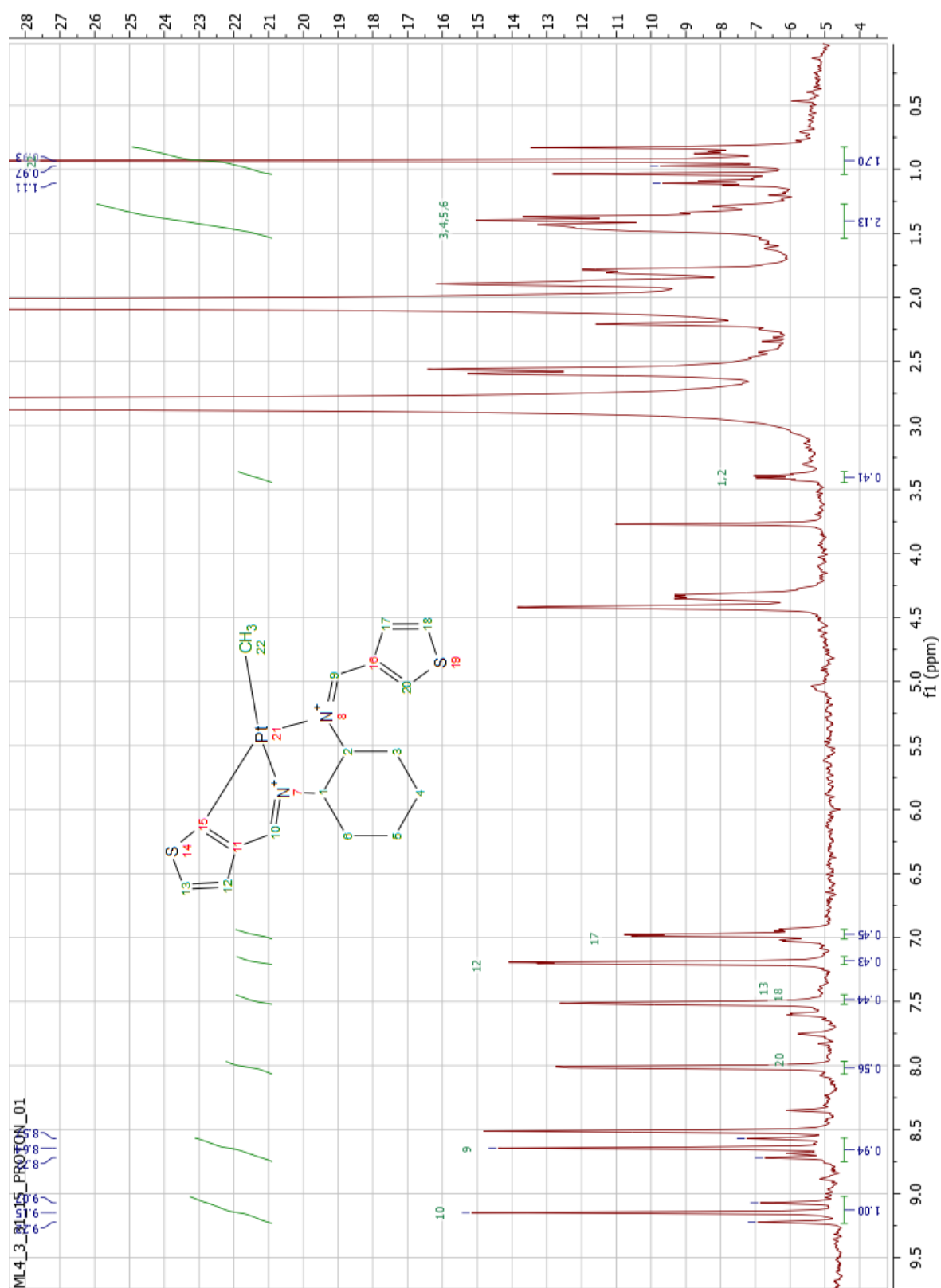


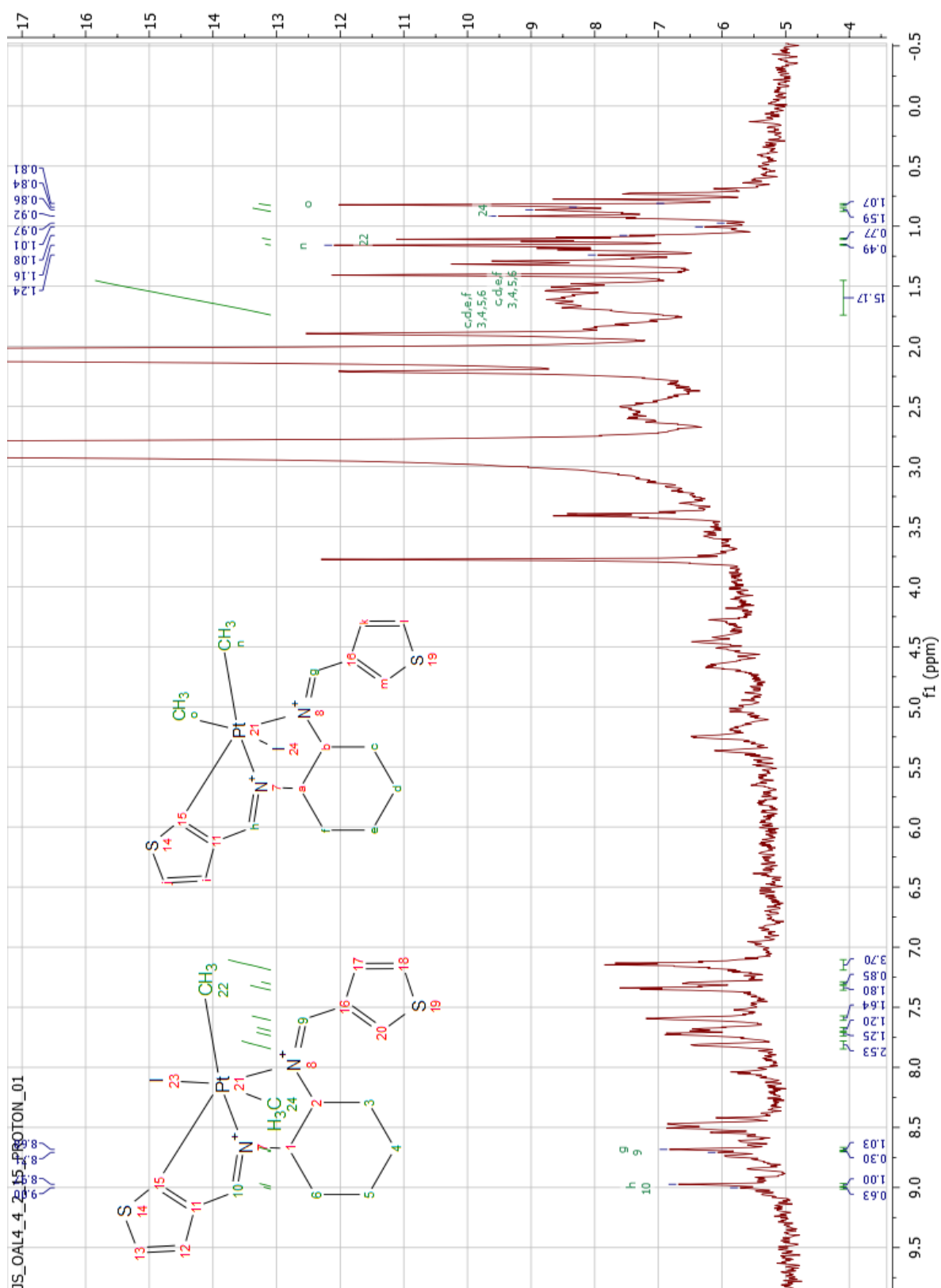


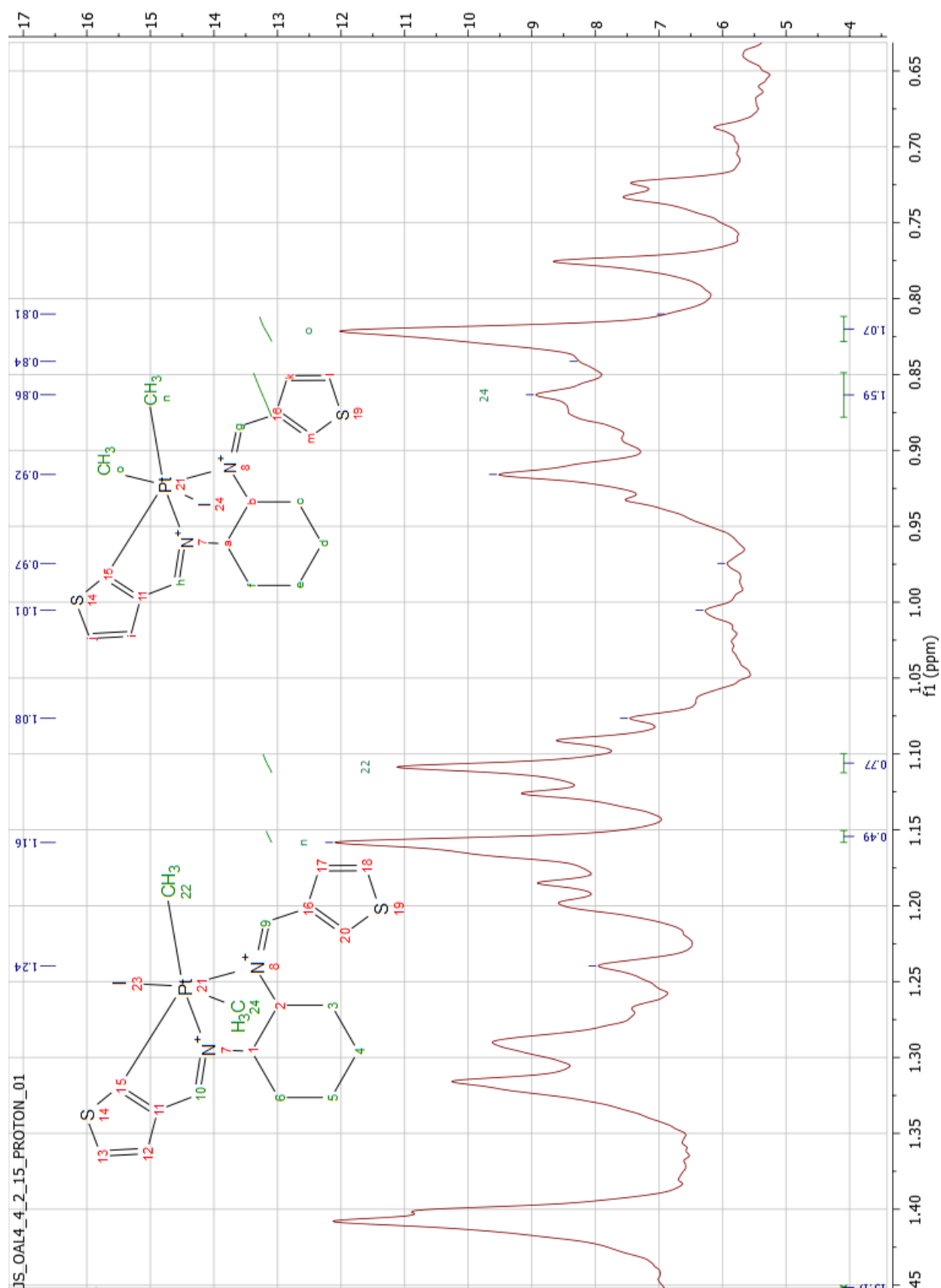


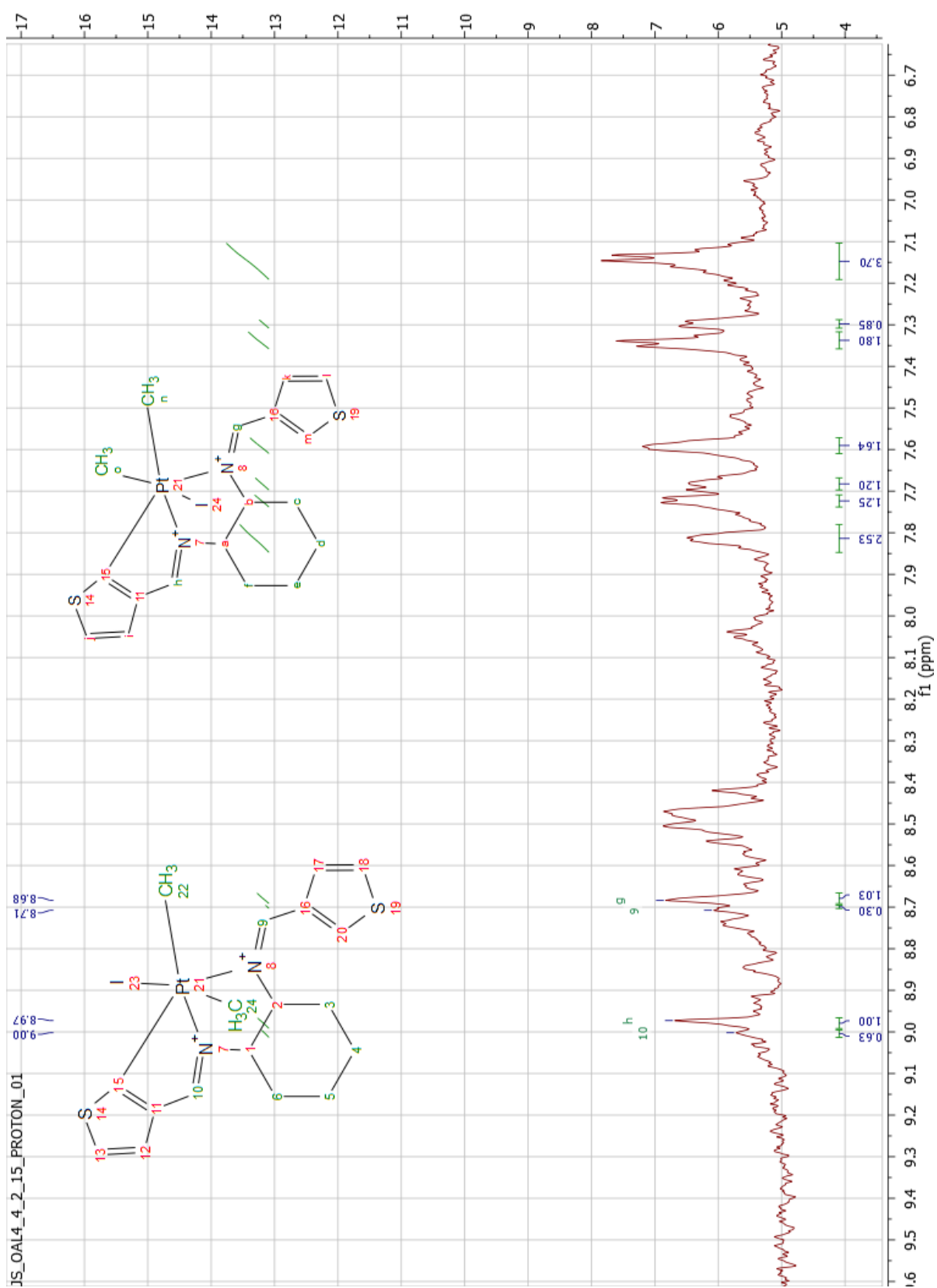






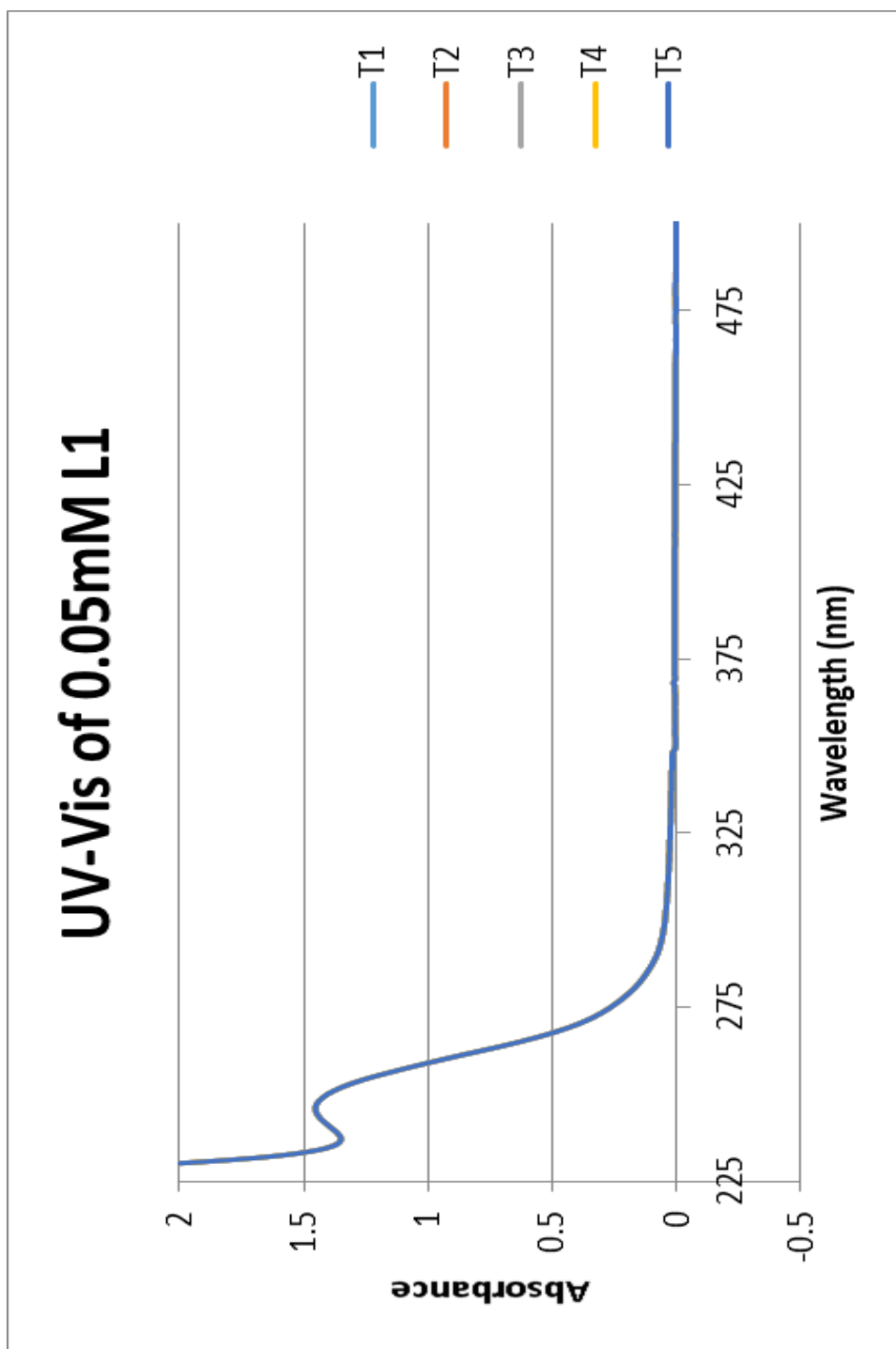


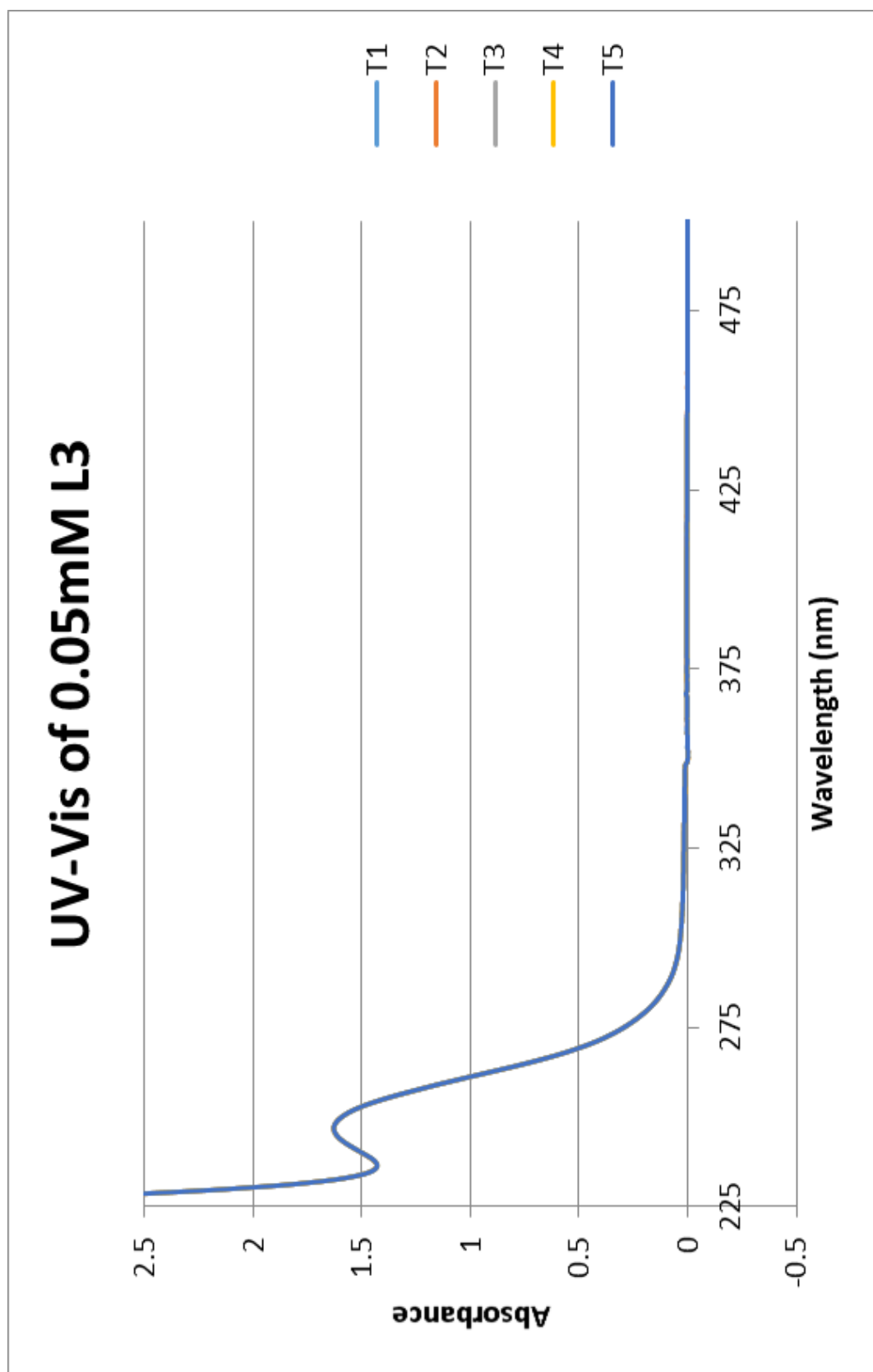


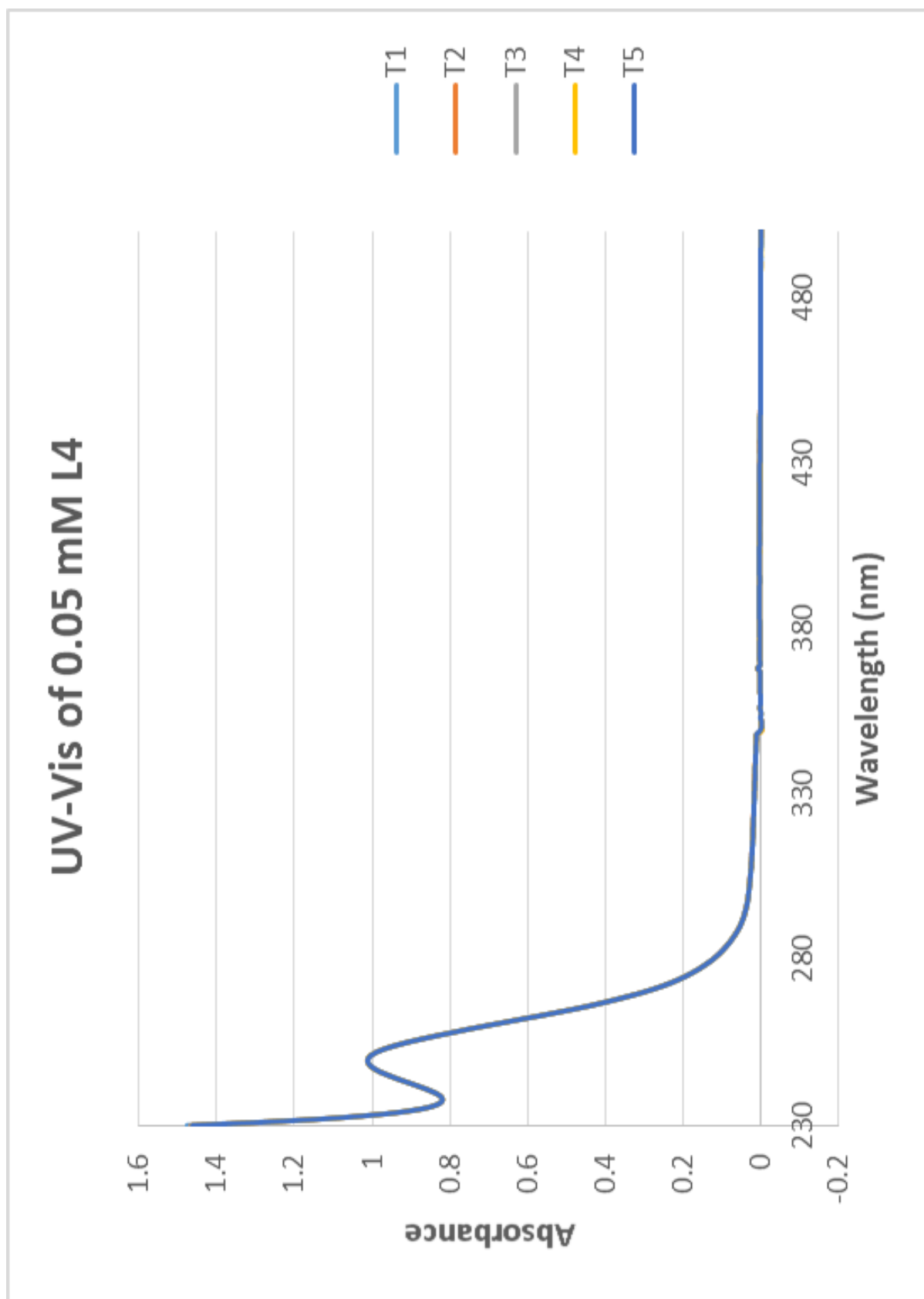


8. Appendix B: UV-Visible Spectrum

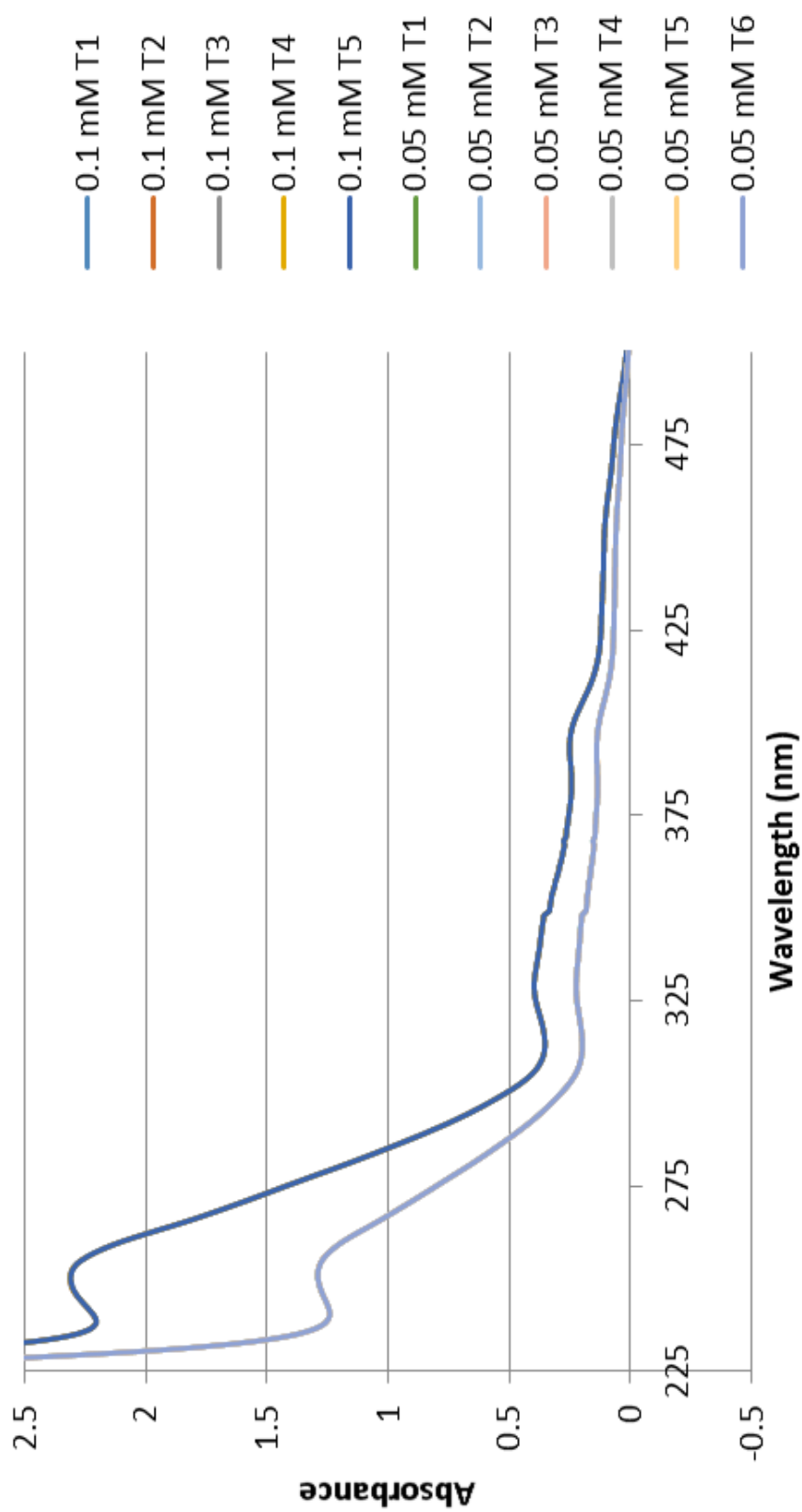
Note: T=trial

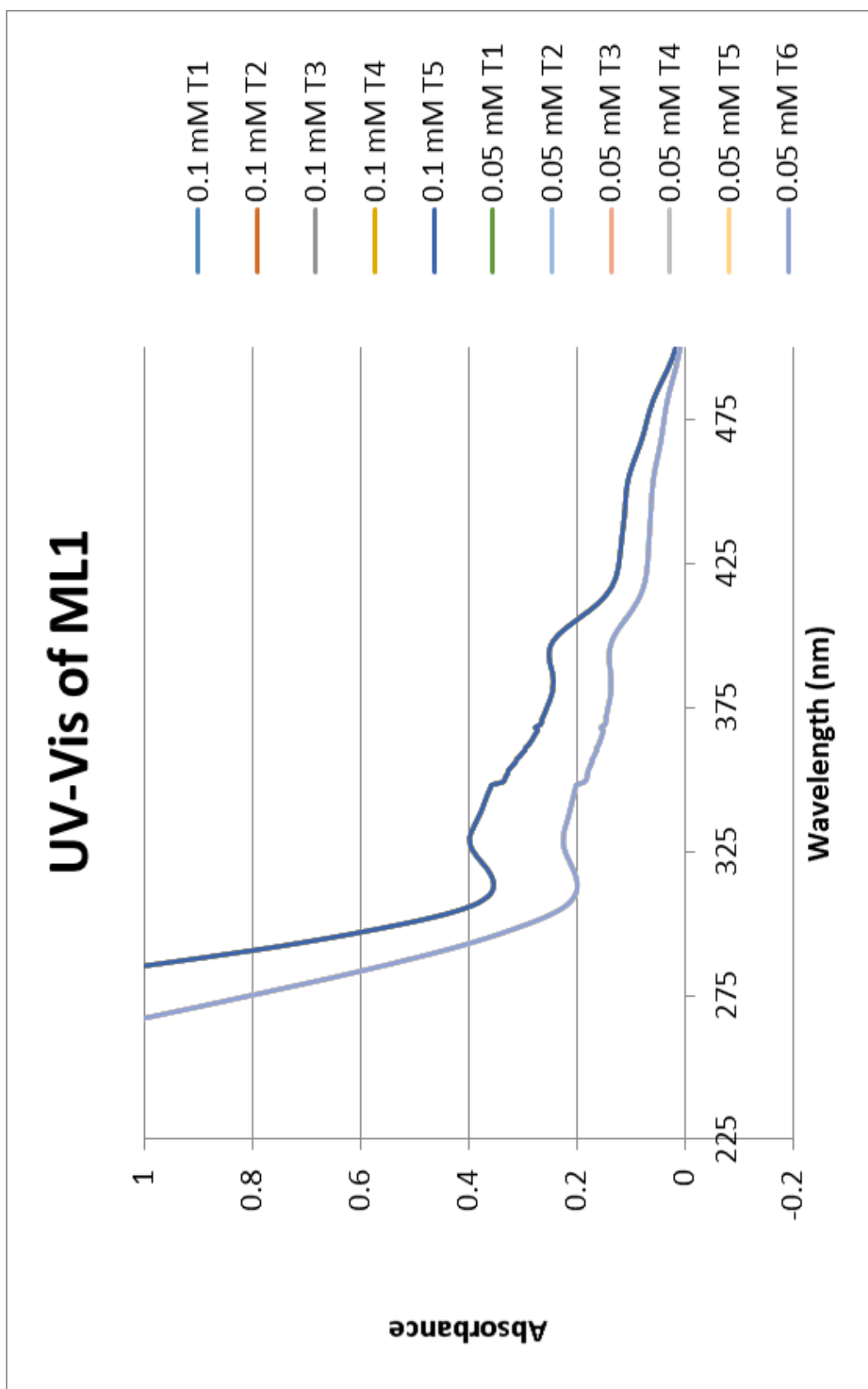




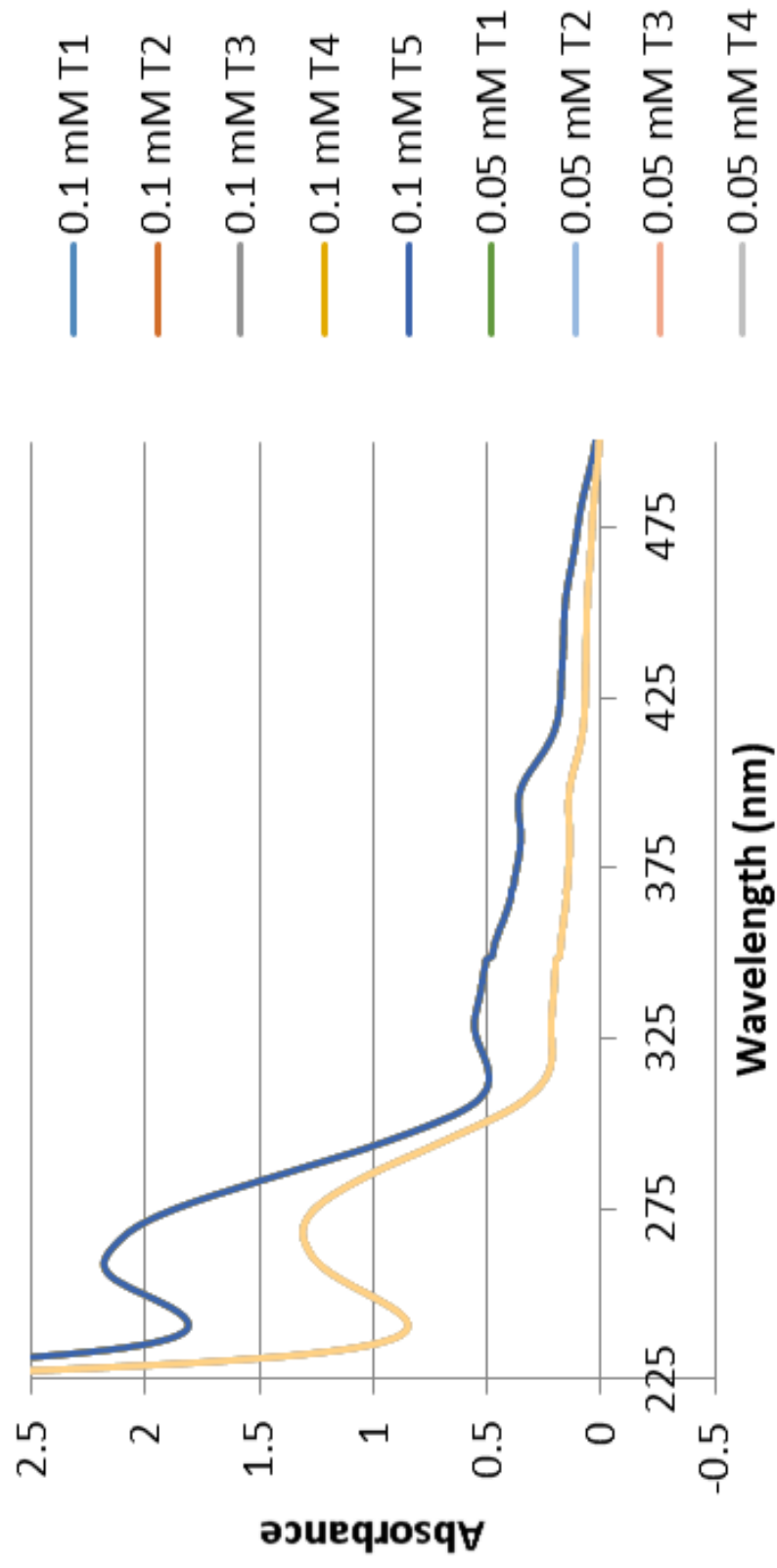


UV-Vis of ML1

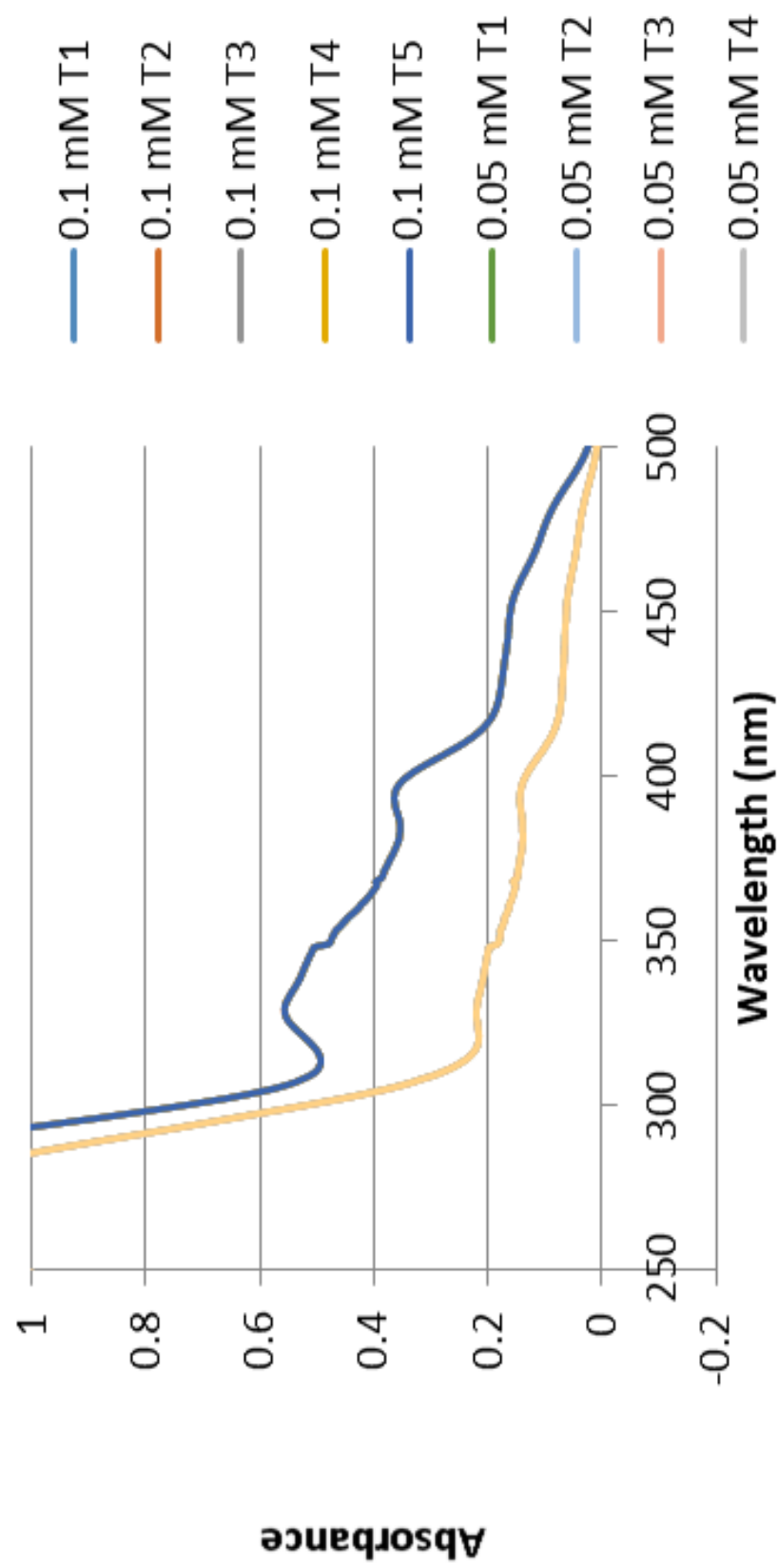


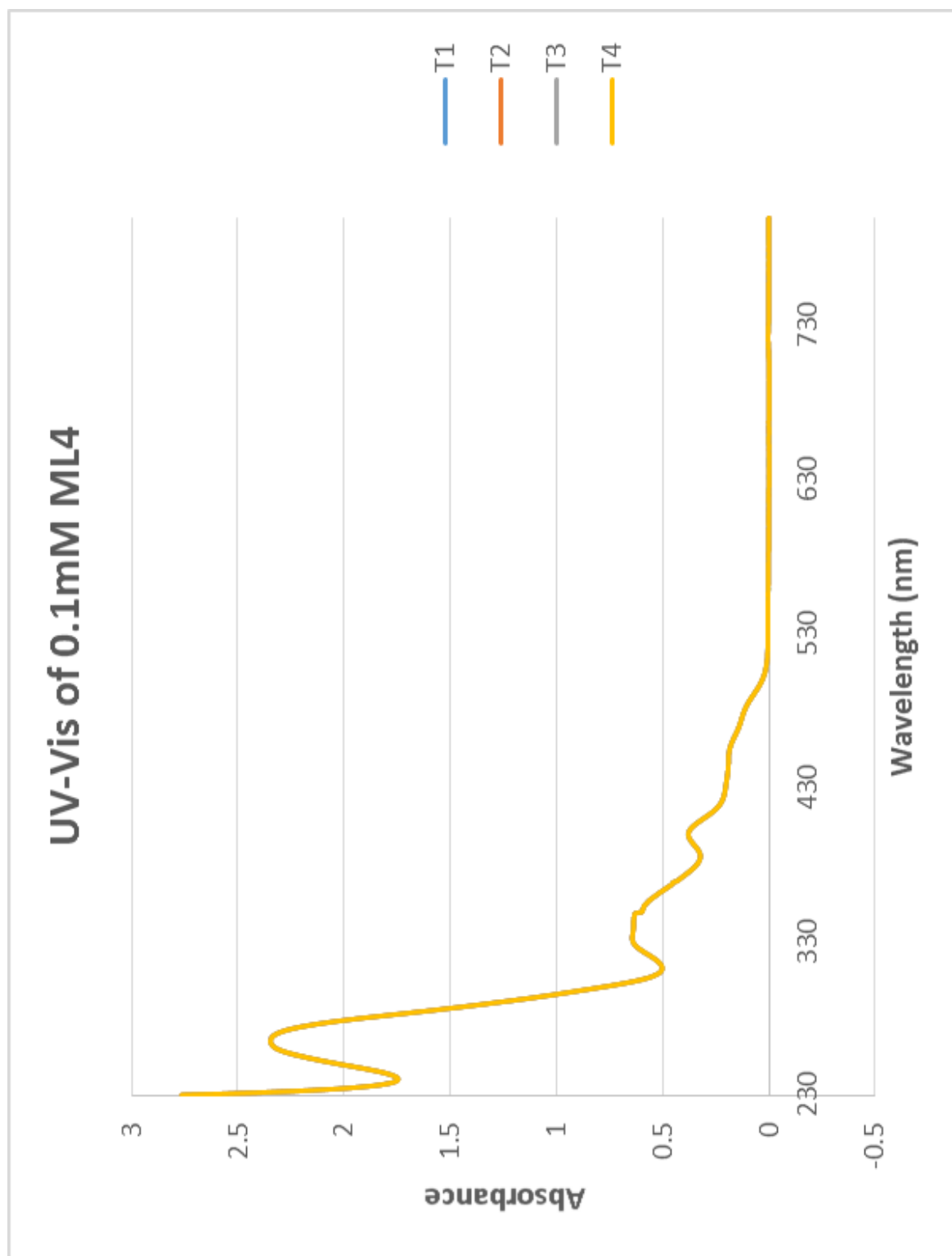


UV Vis of ML3



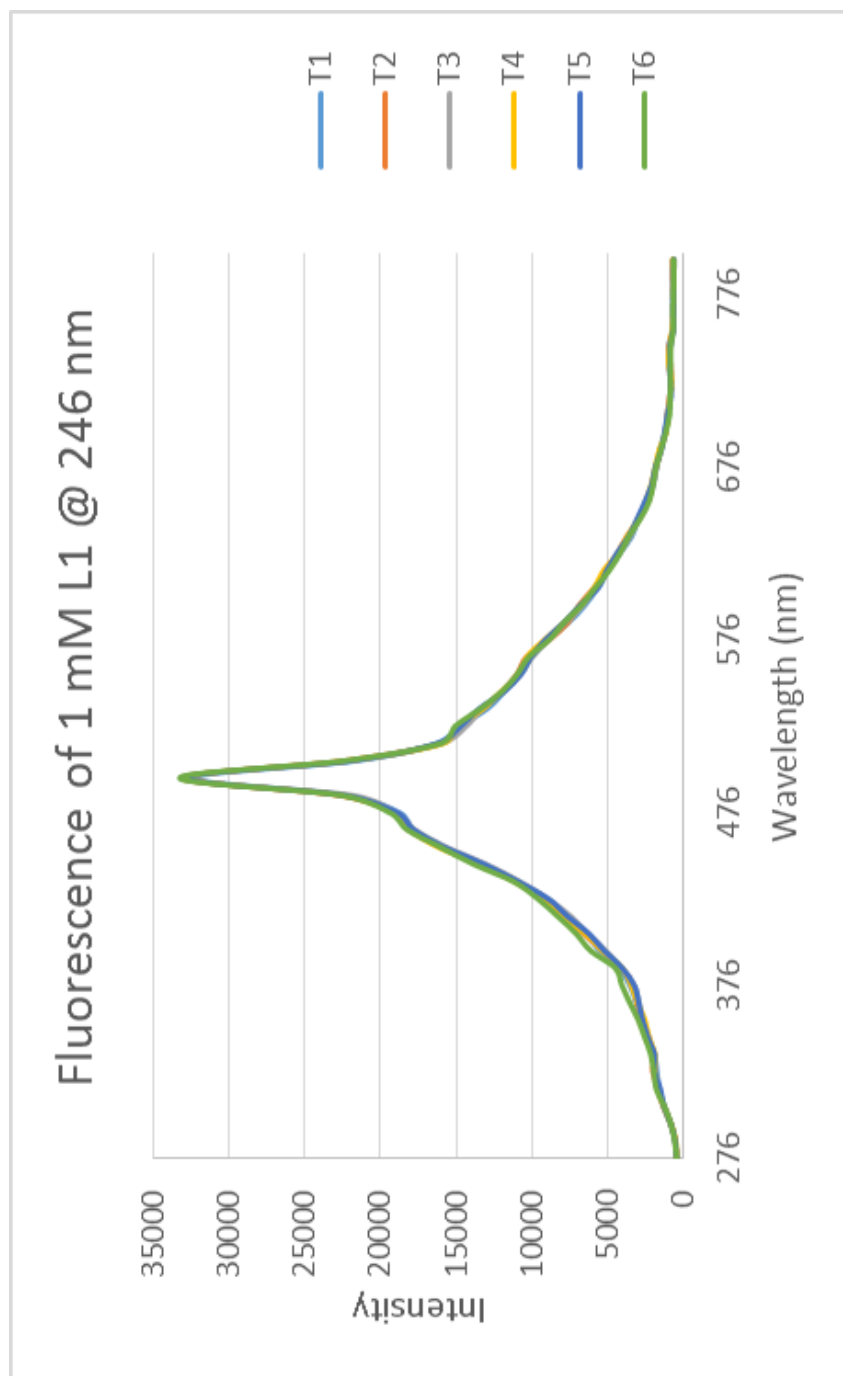
UV Vis of ML3

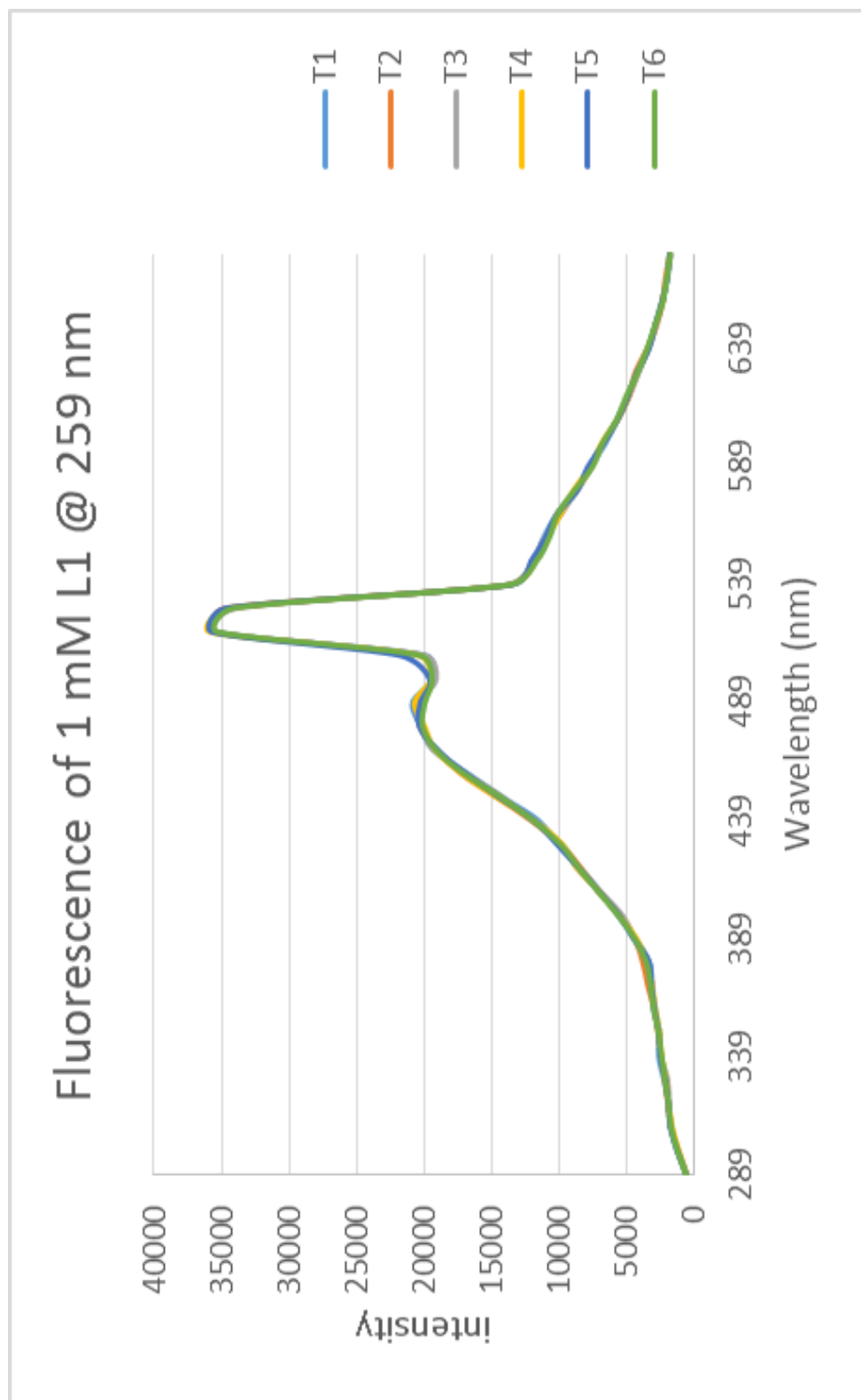


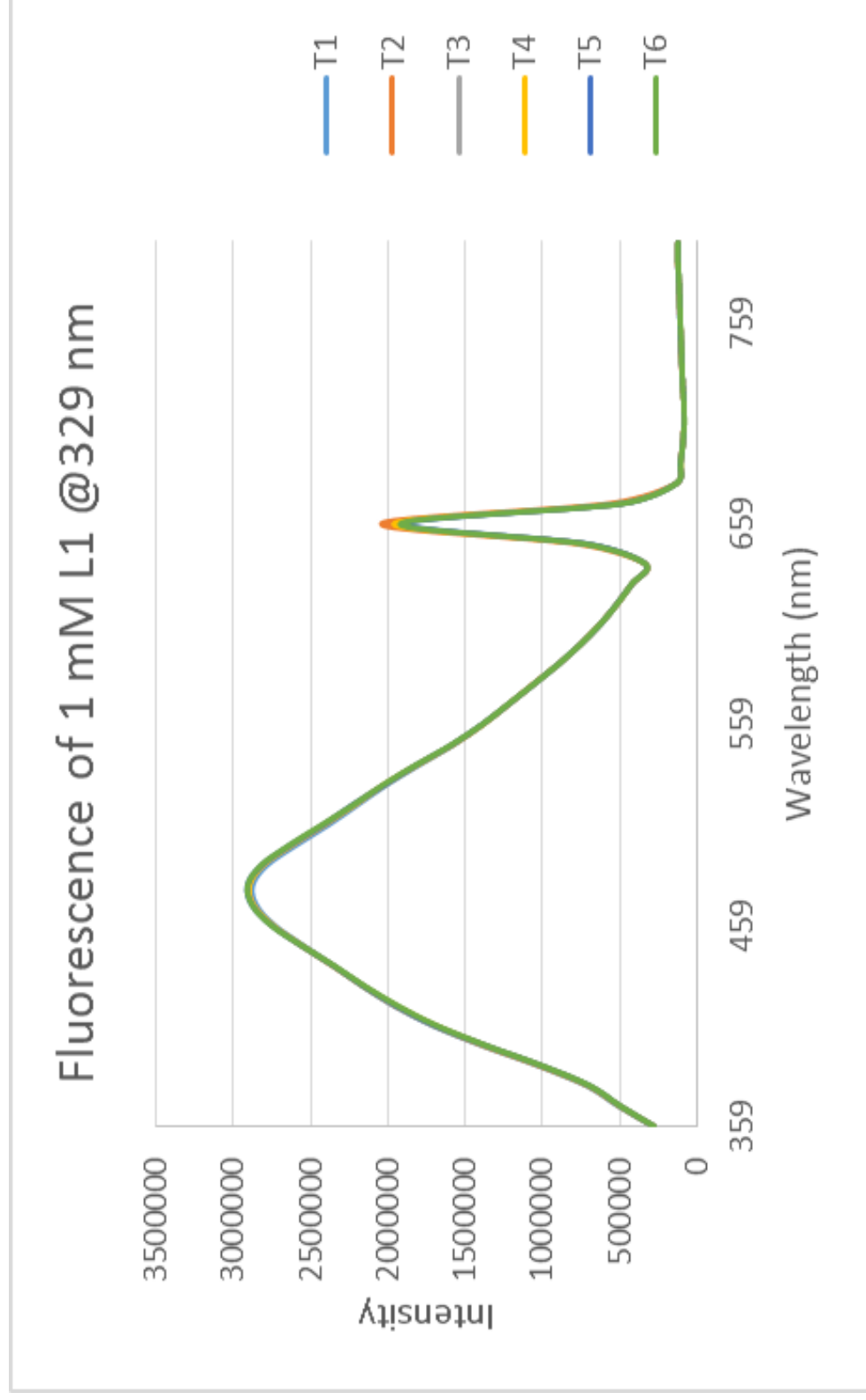


9. Appendix C: Emission Spectrum

***Note: T=trial; Emission spectra at other wavelengths for ligands (L1, L3, and L4) were to confirm ML emissions**



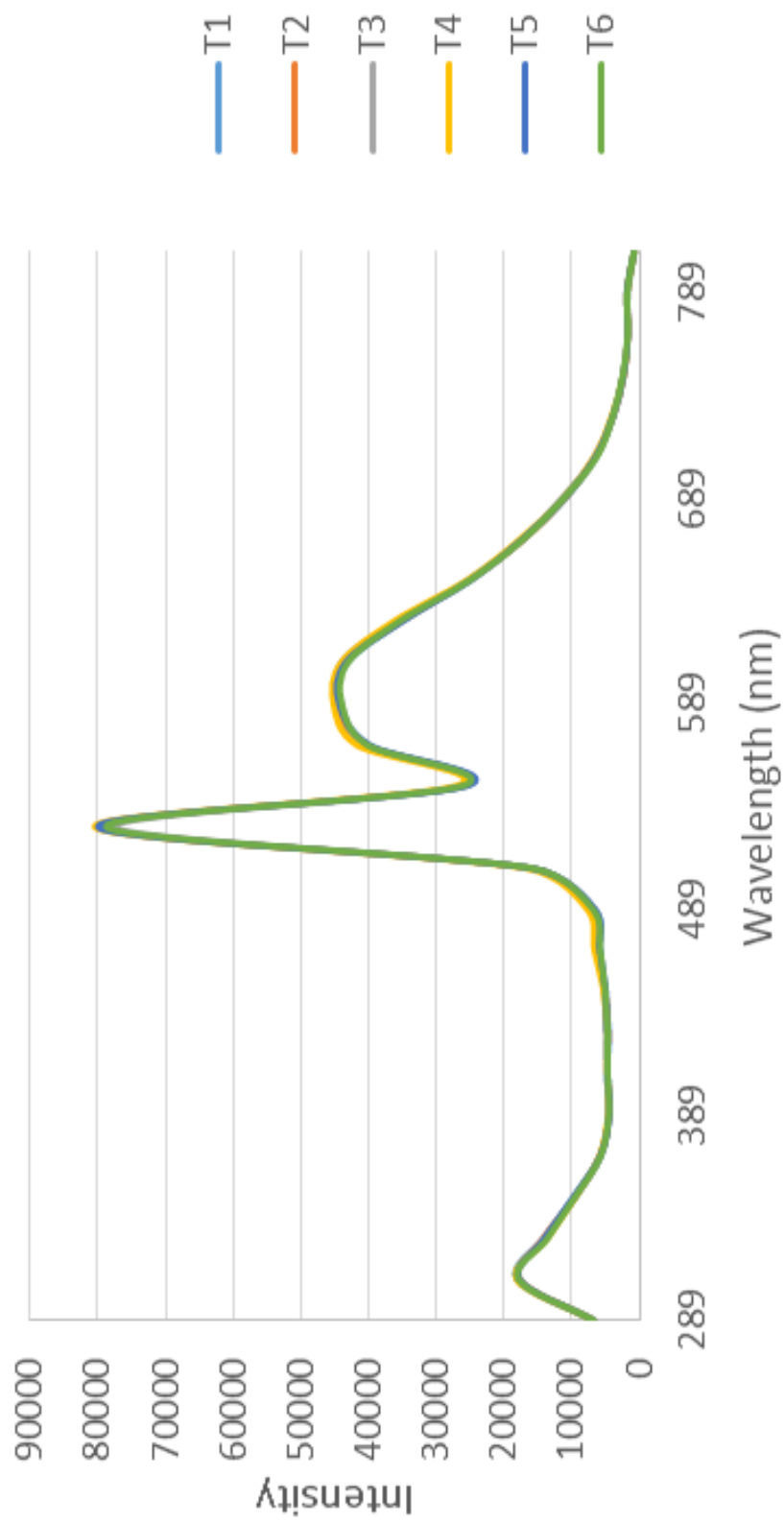


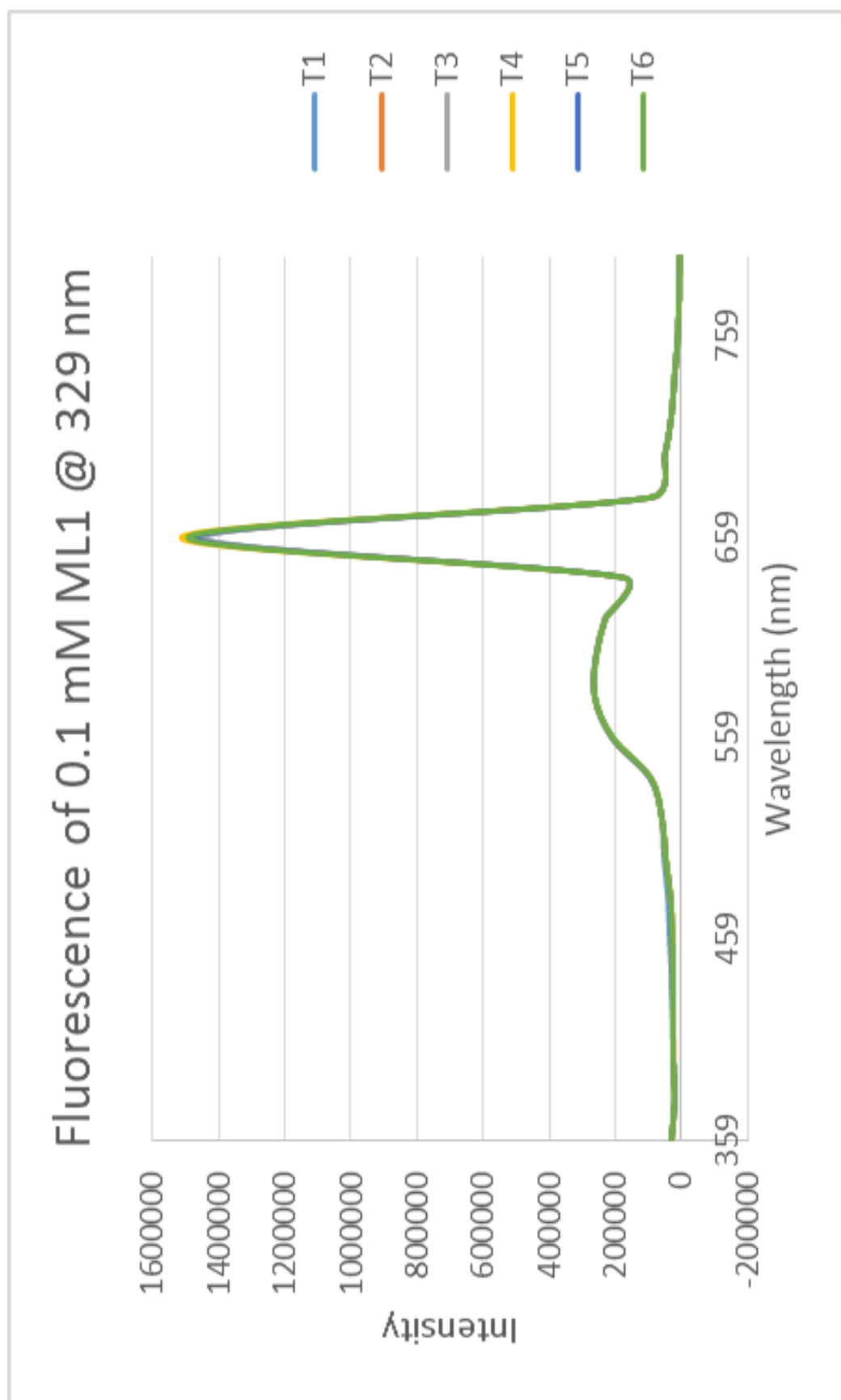


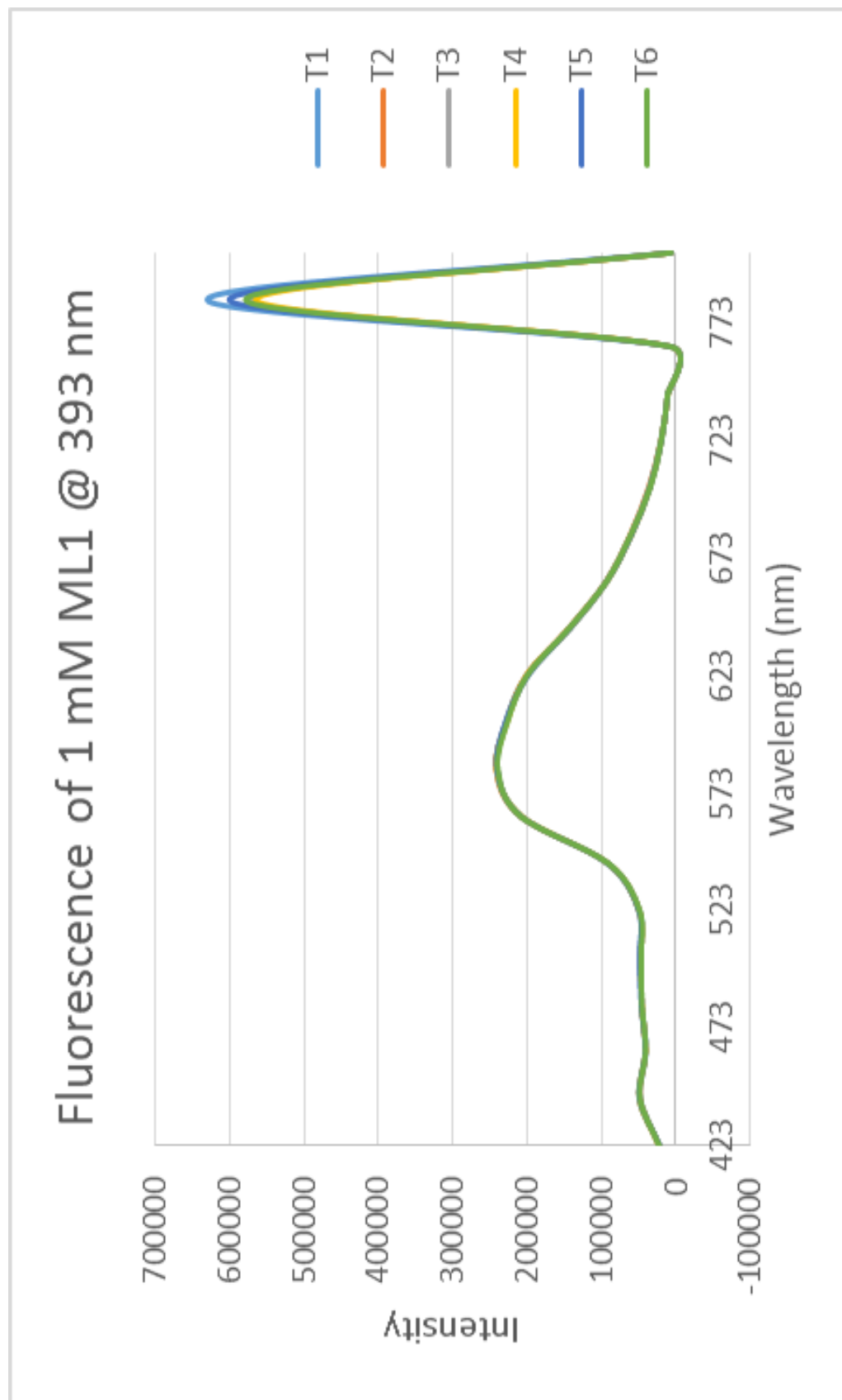
Fluorescence of 1 mM L1 @ 393 nm

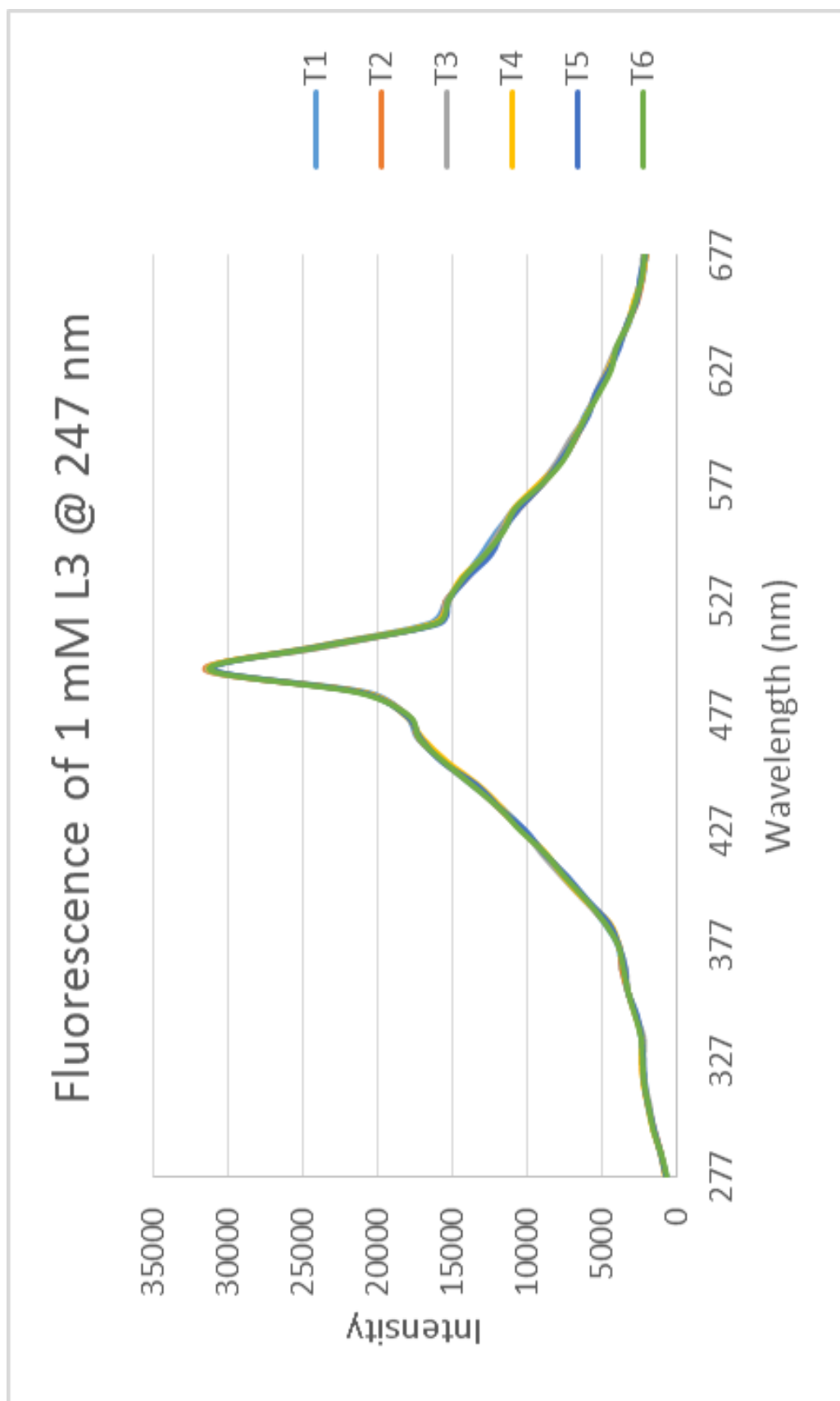


Fluorescence of 0.1 mM ML1 @ 259 nm

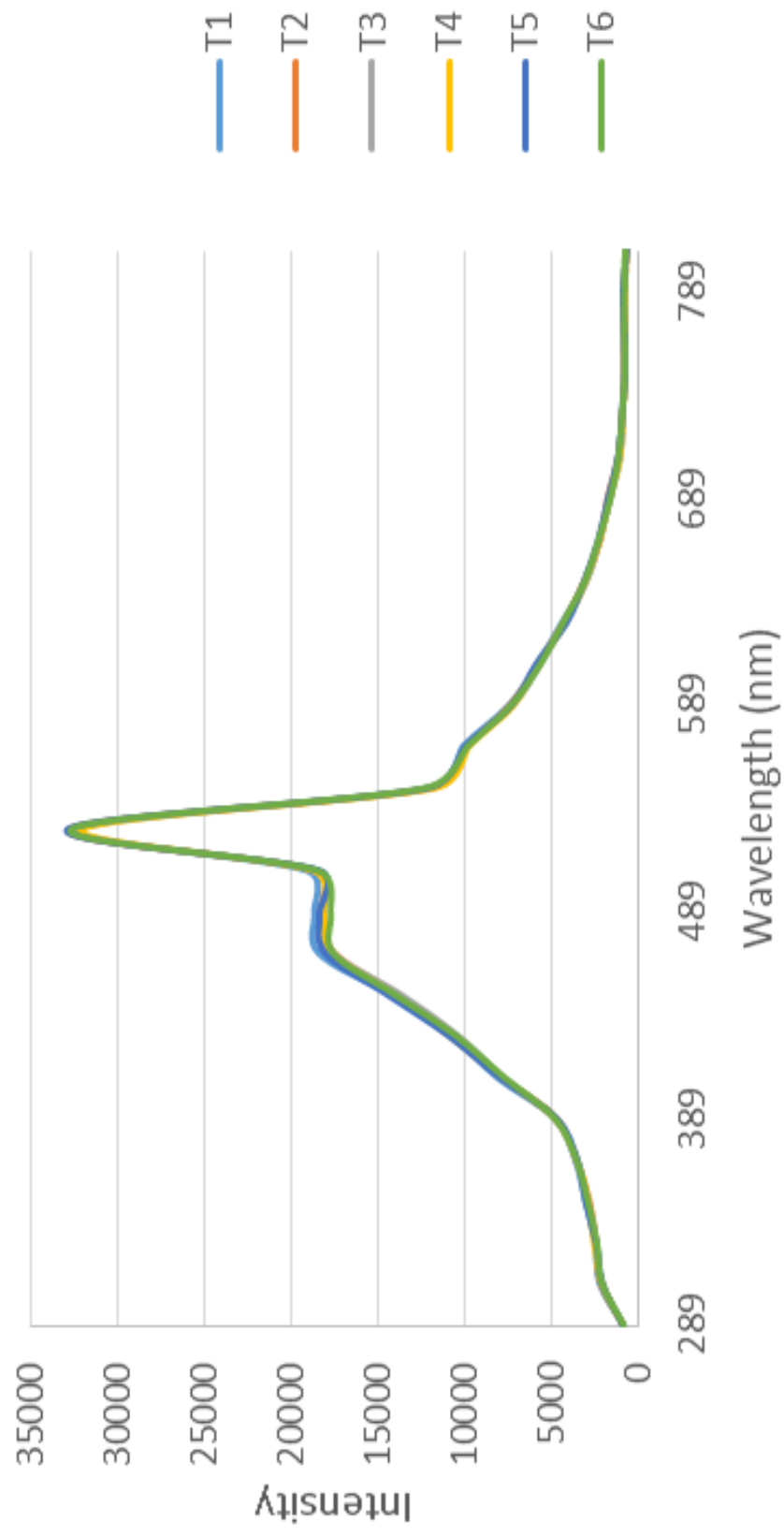




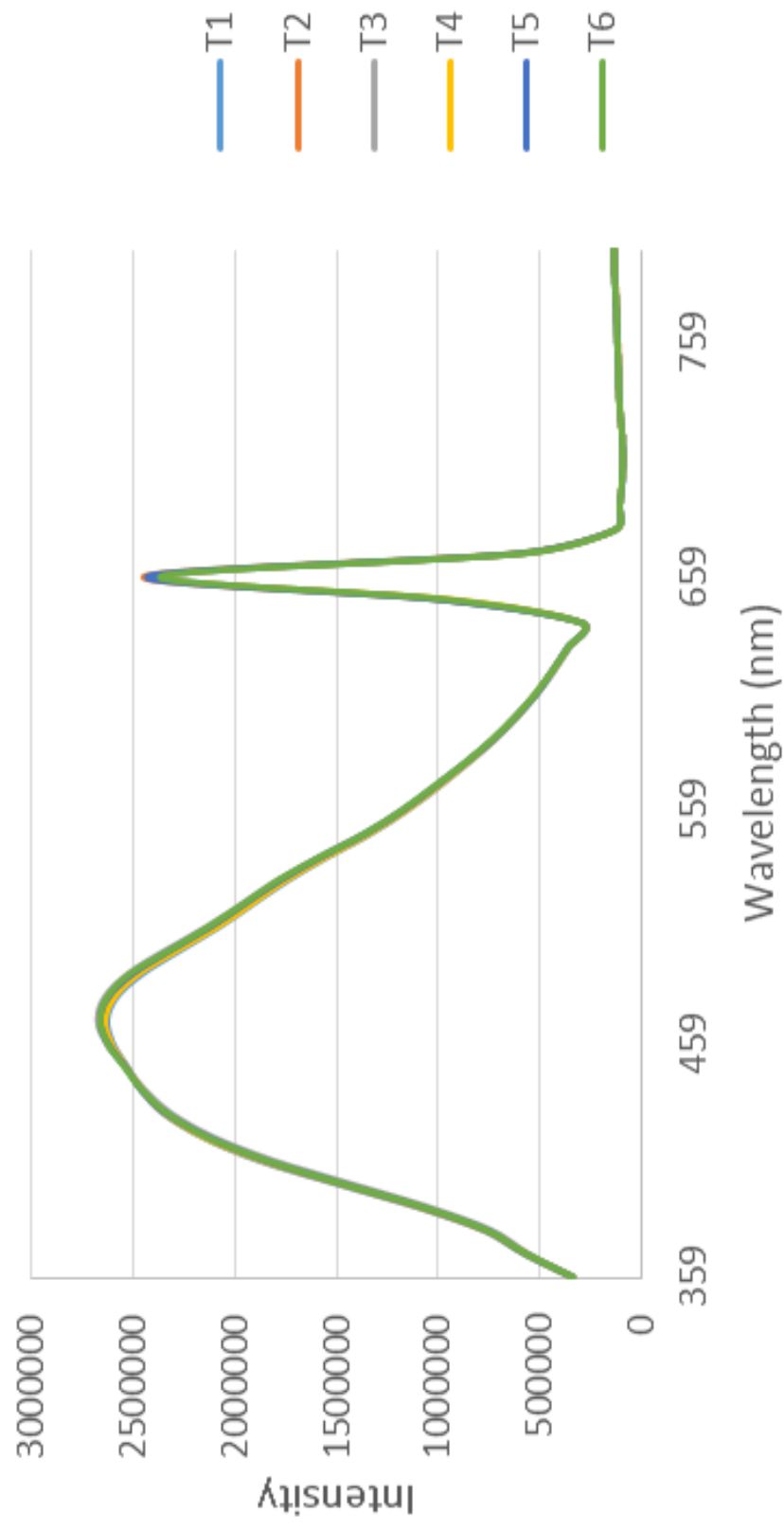


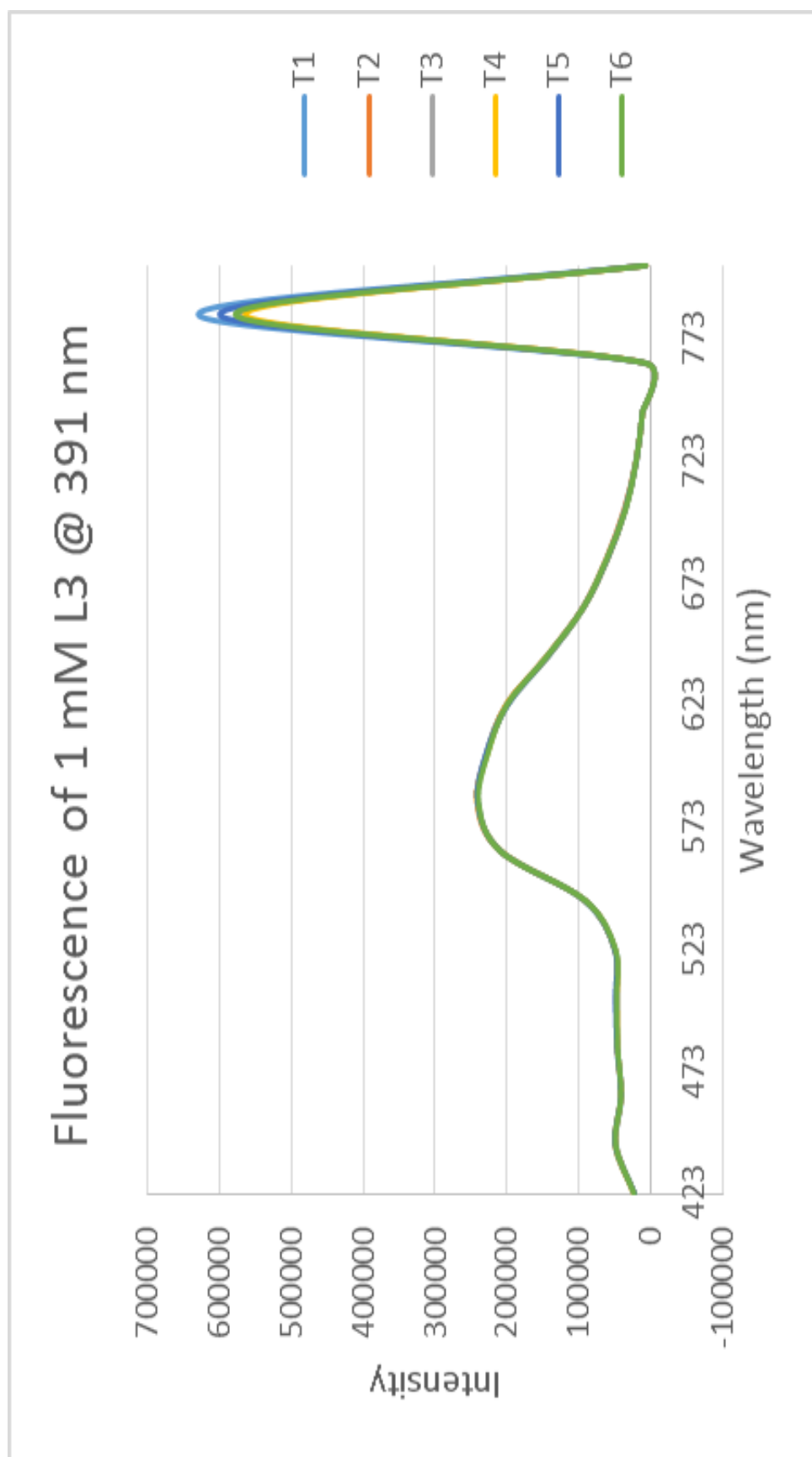


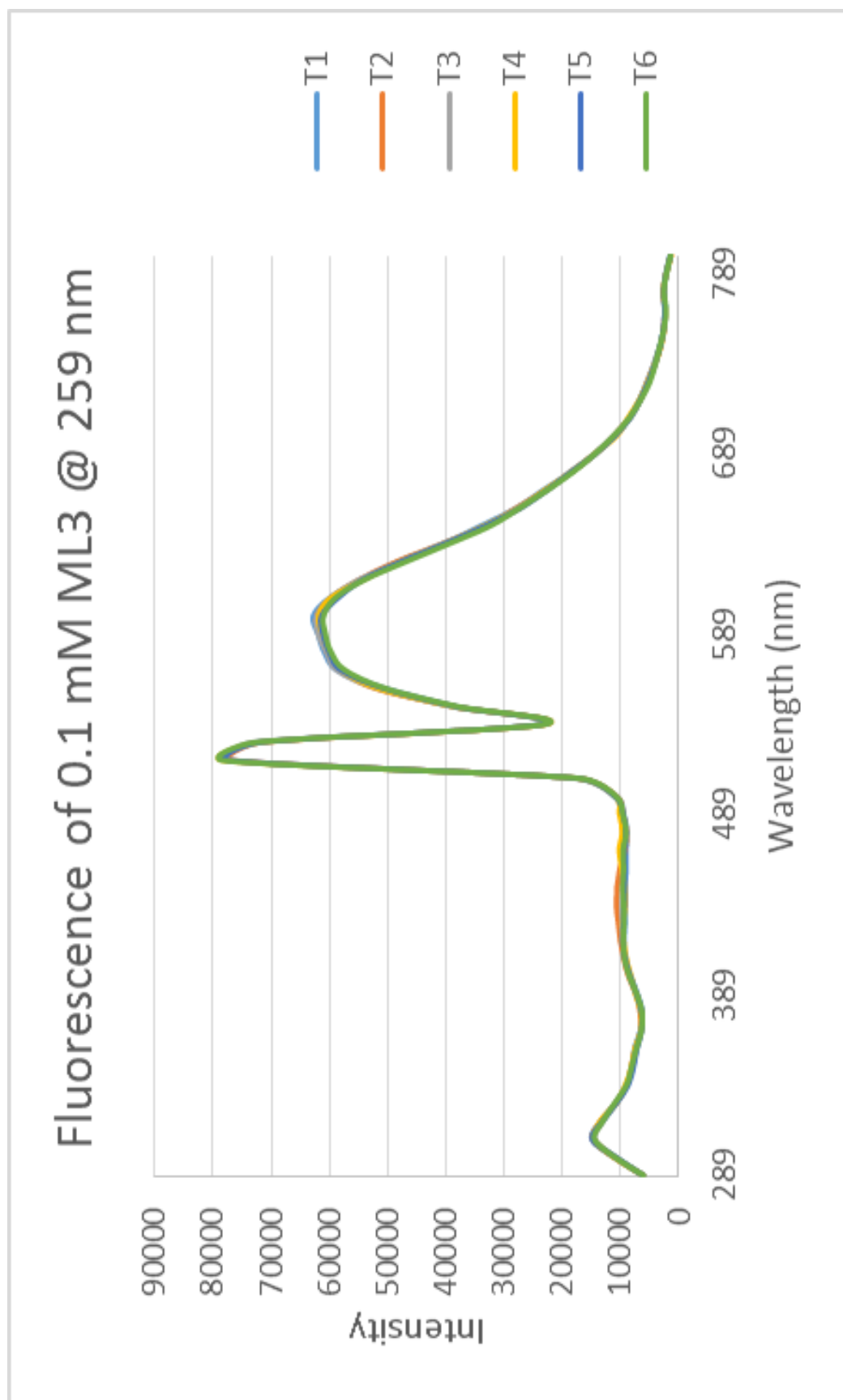
Fluorescence of 1 mM L3 @ 259 nm

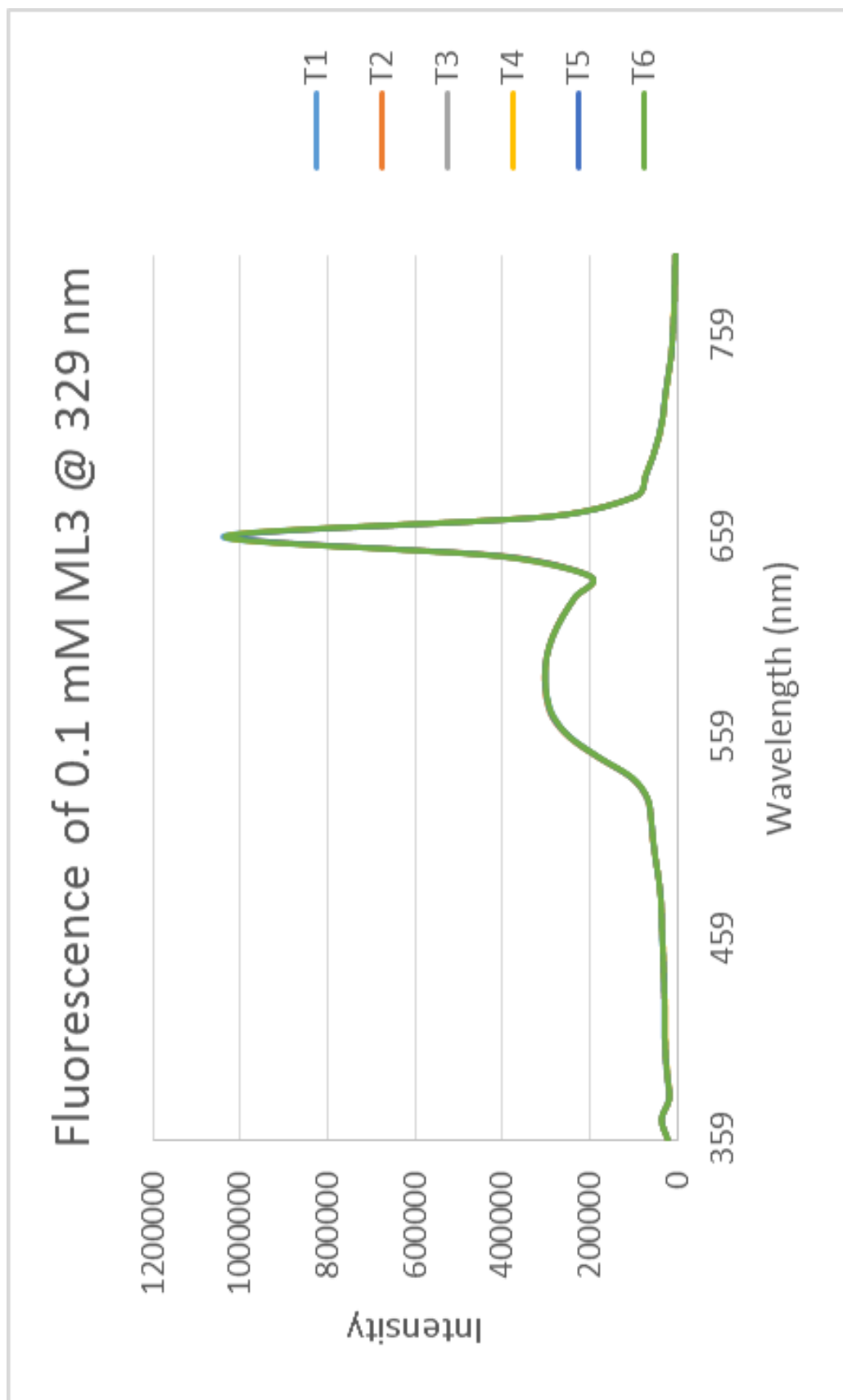


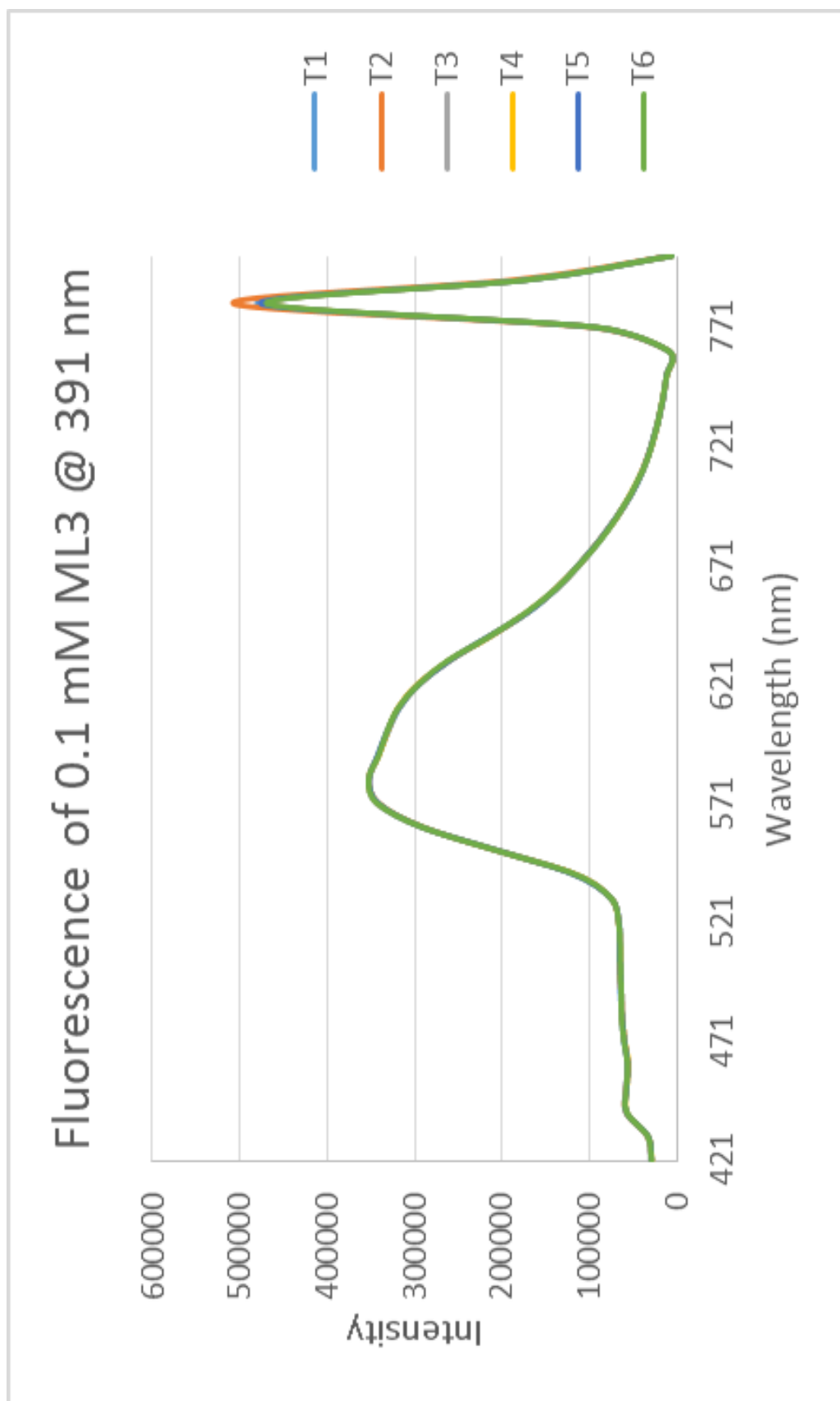
Fluorescence of 1 mM ML3 @ 329 nm

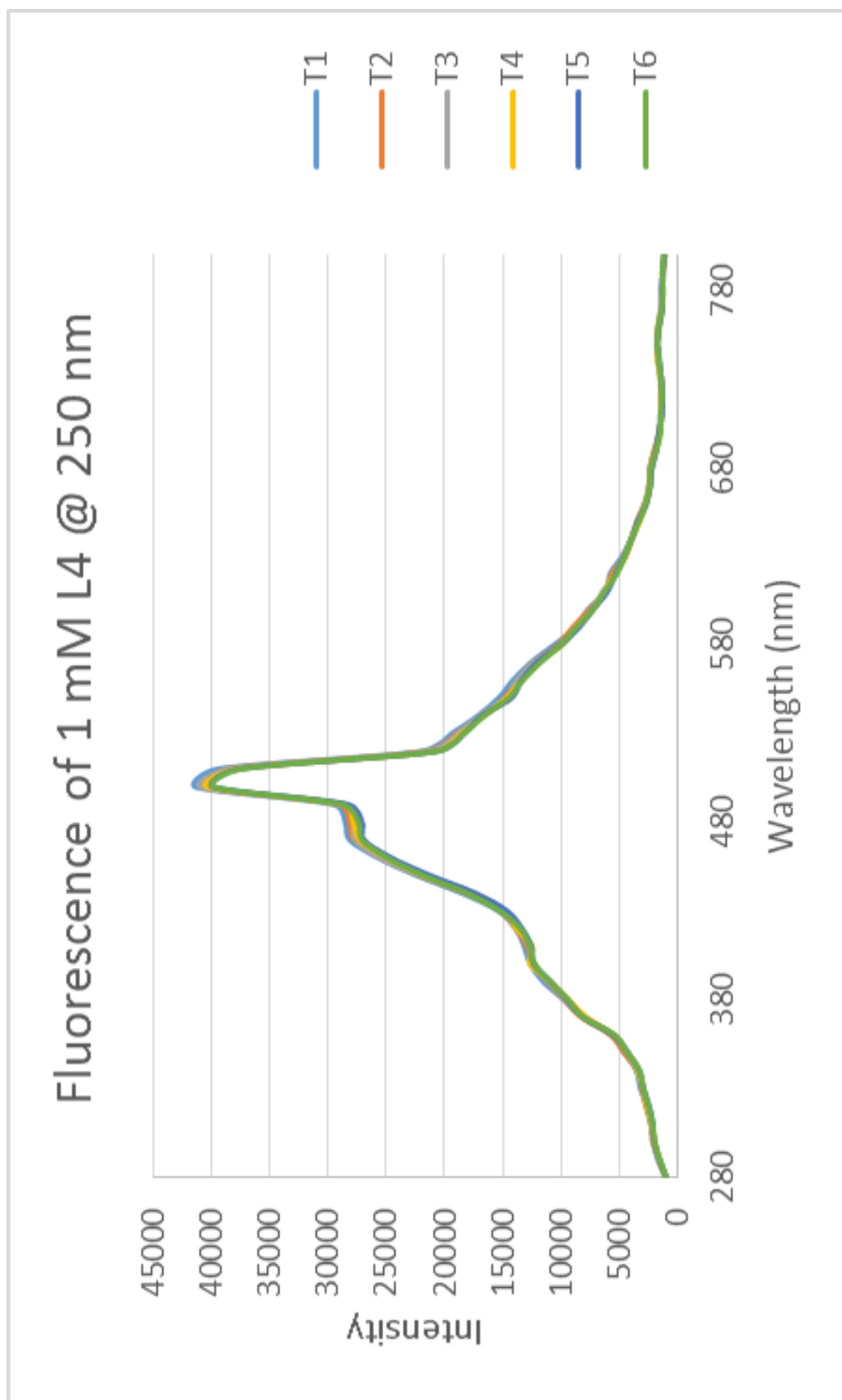






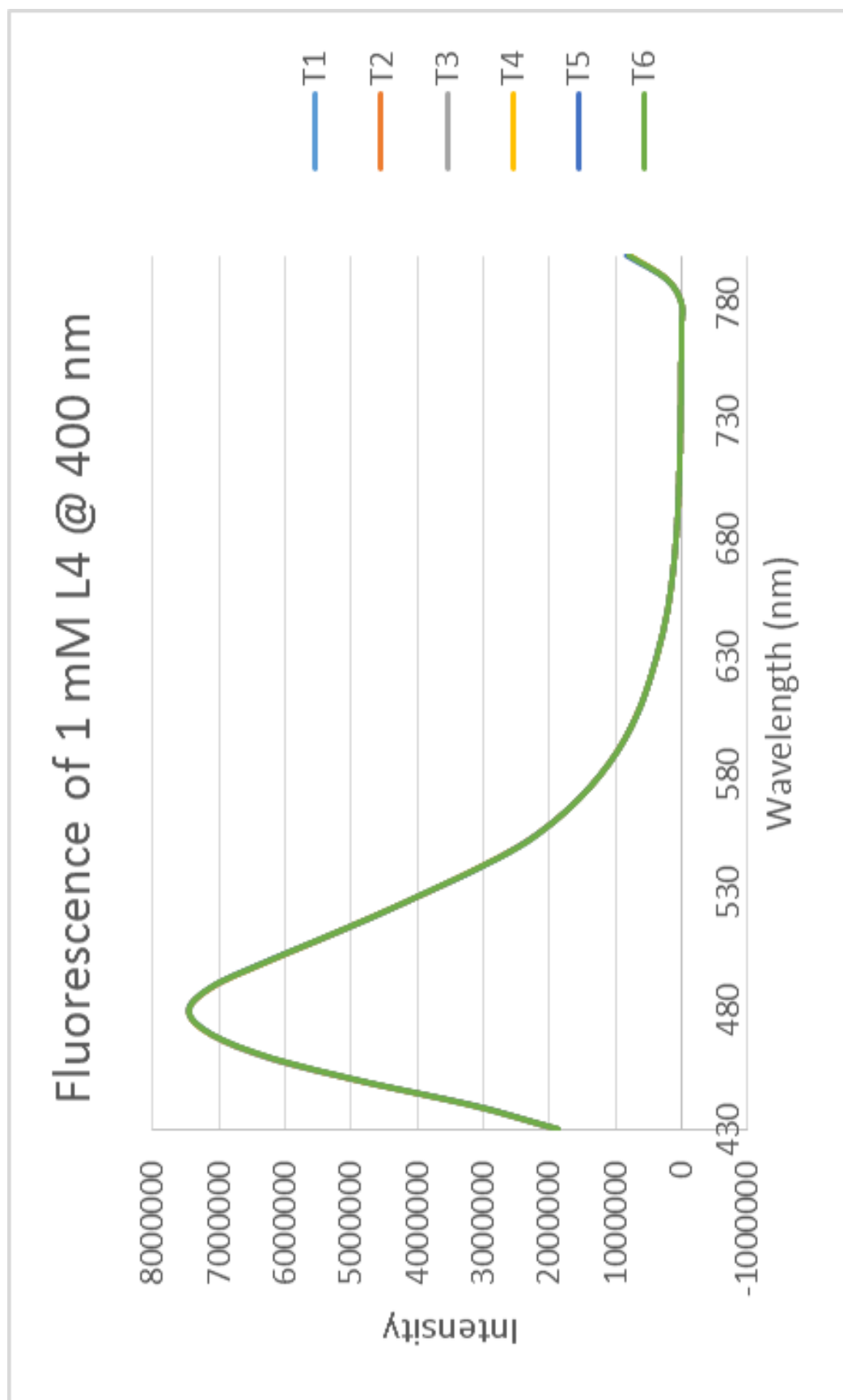


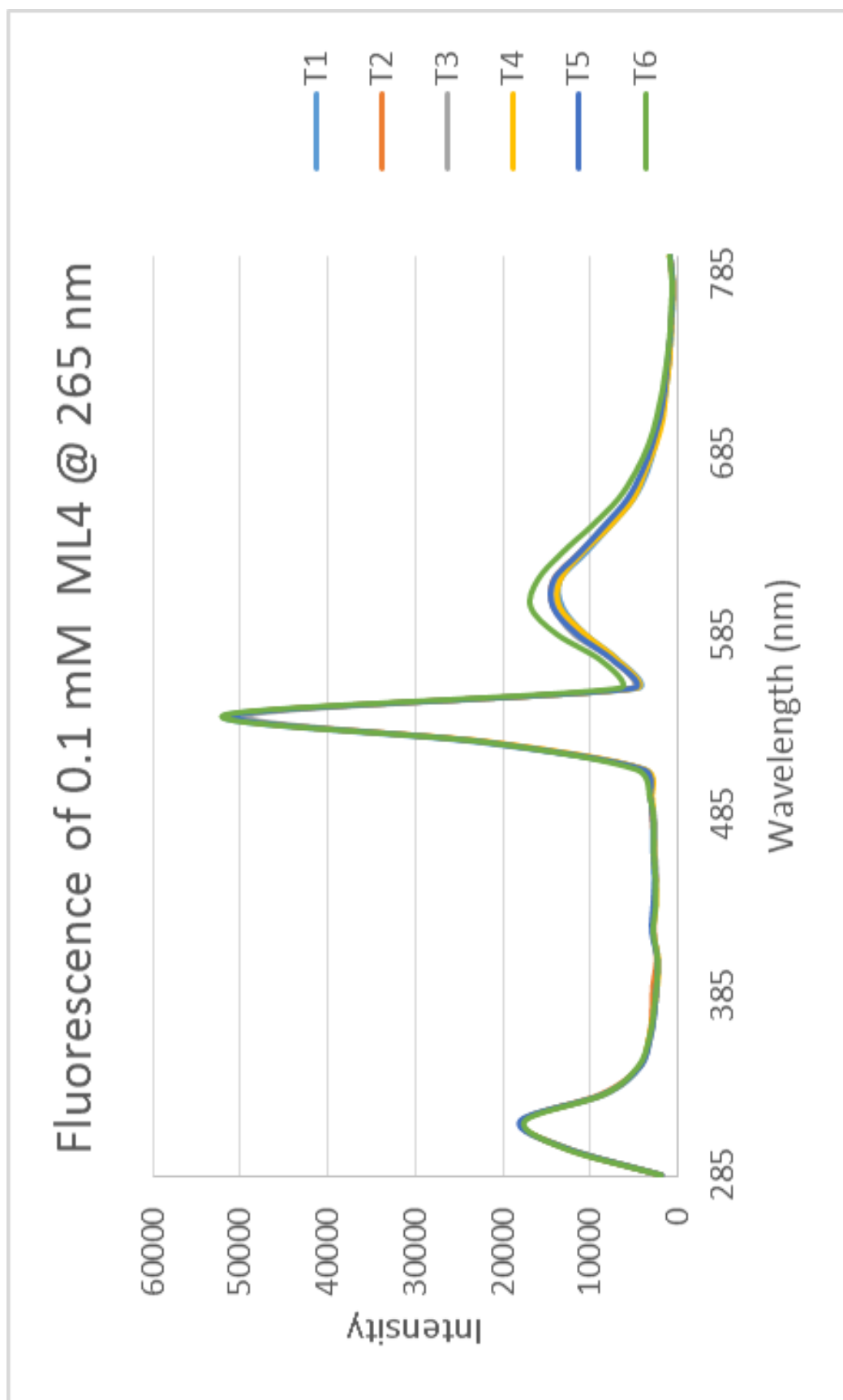




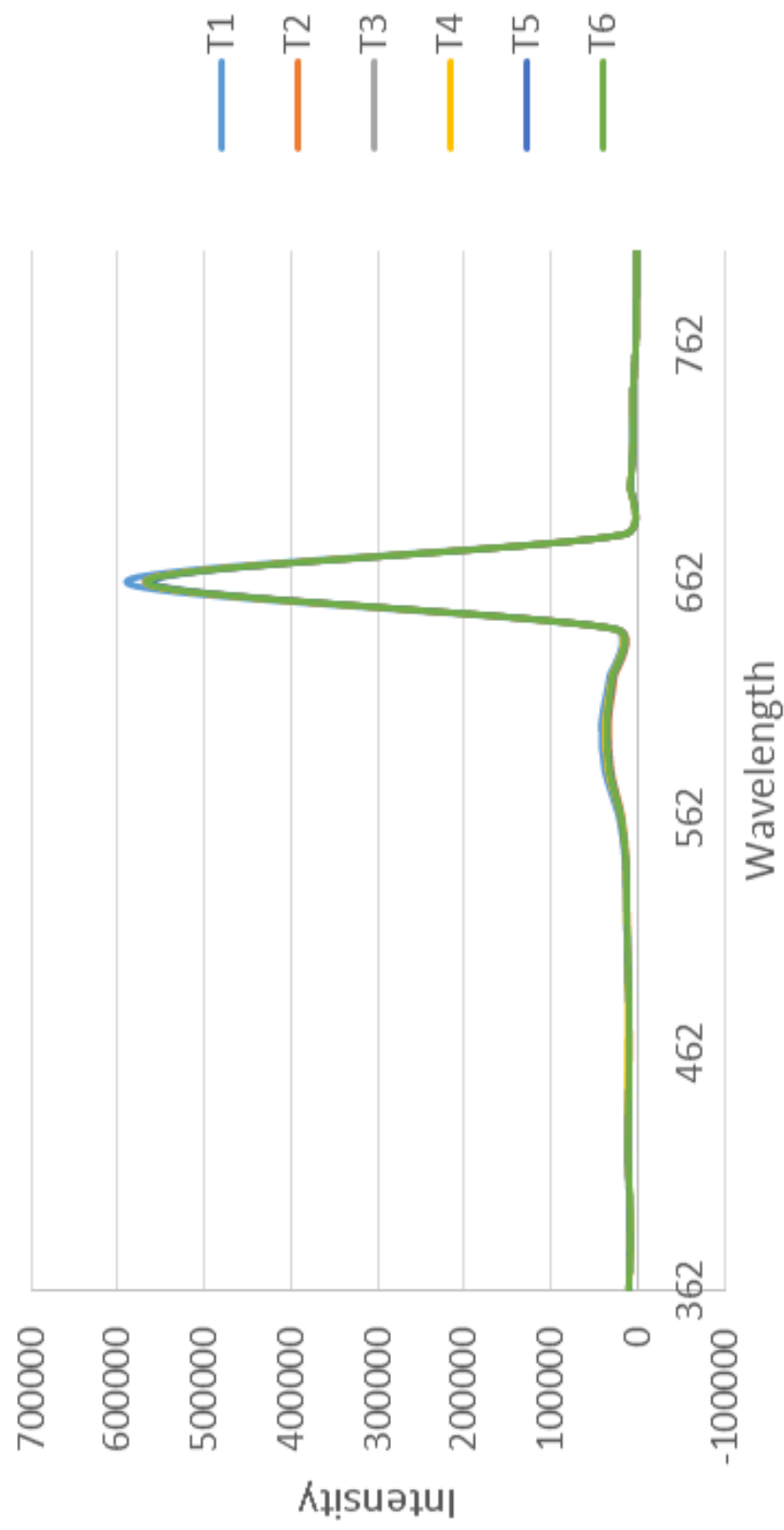


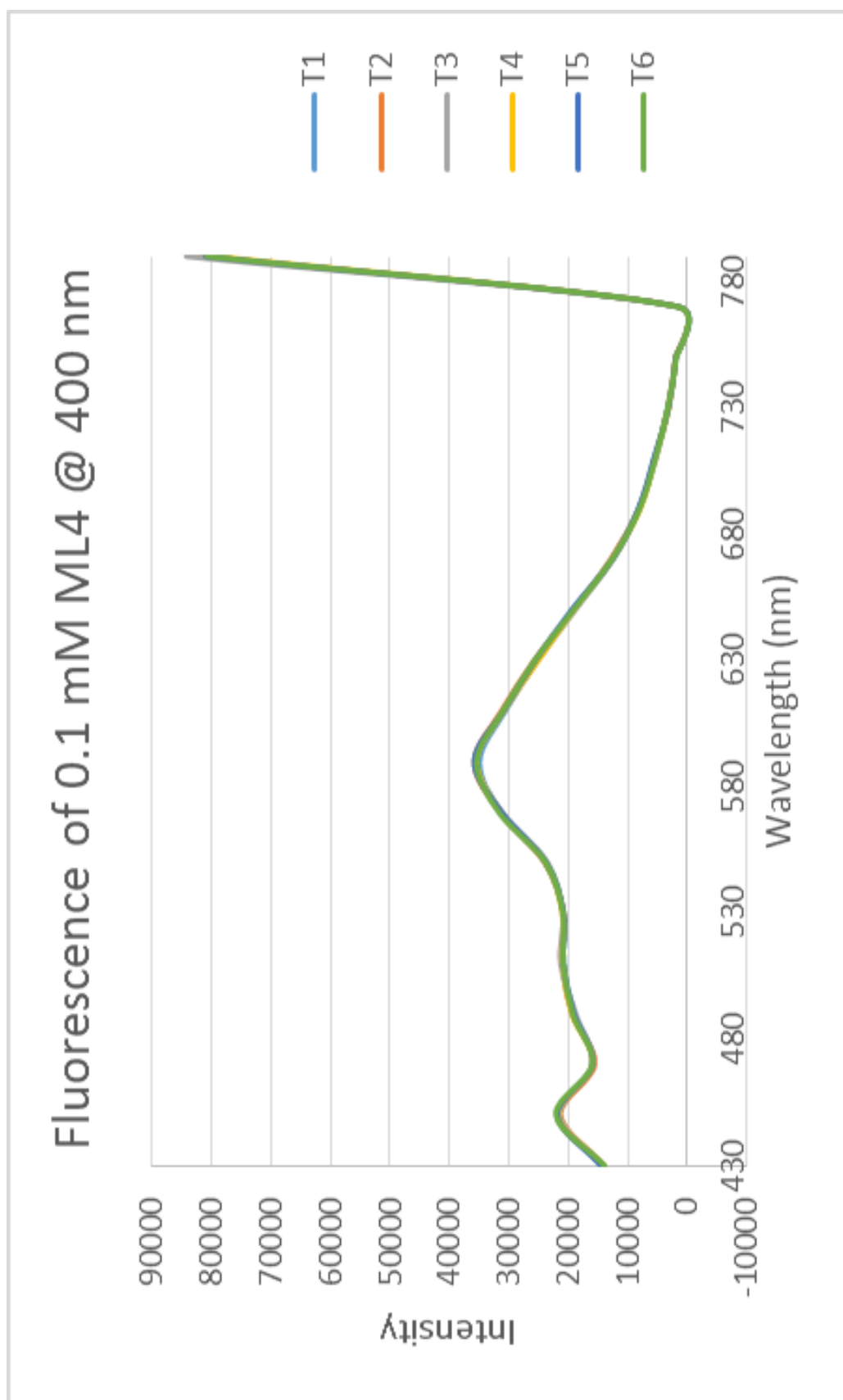




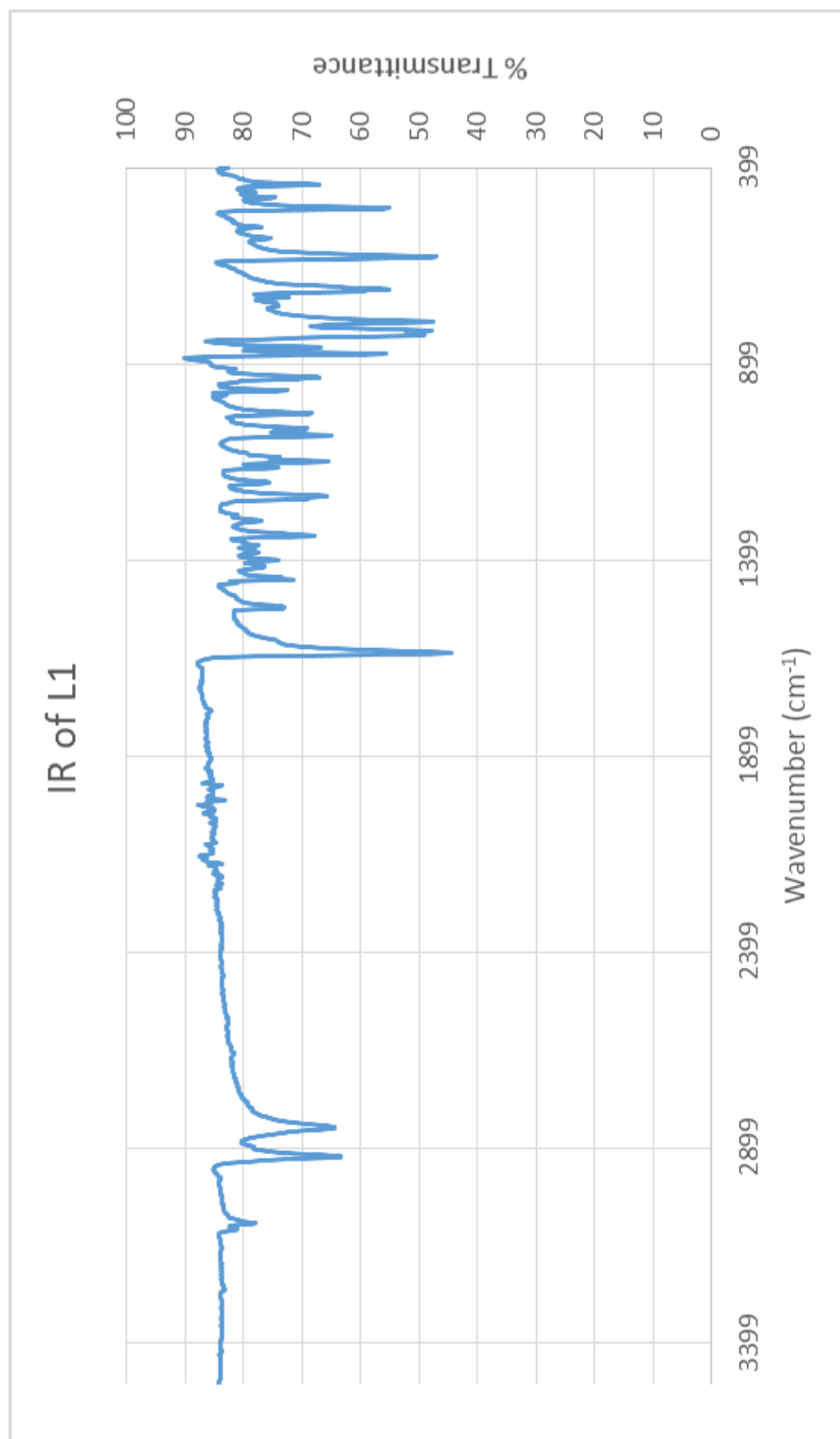


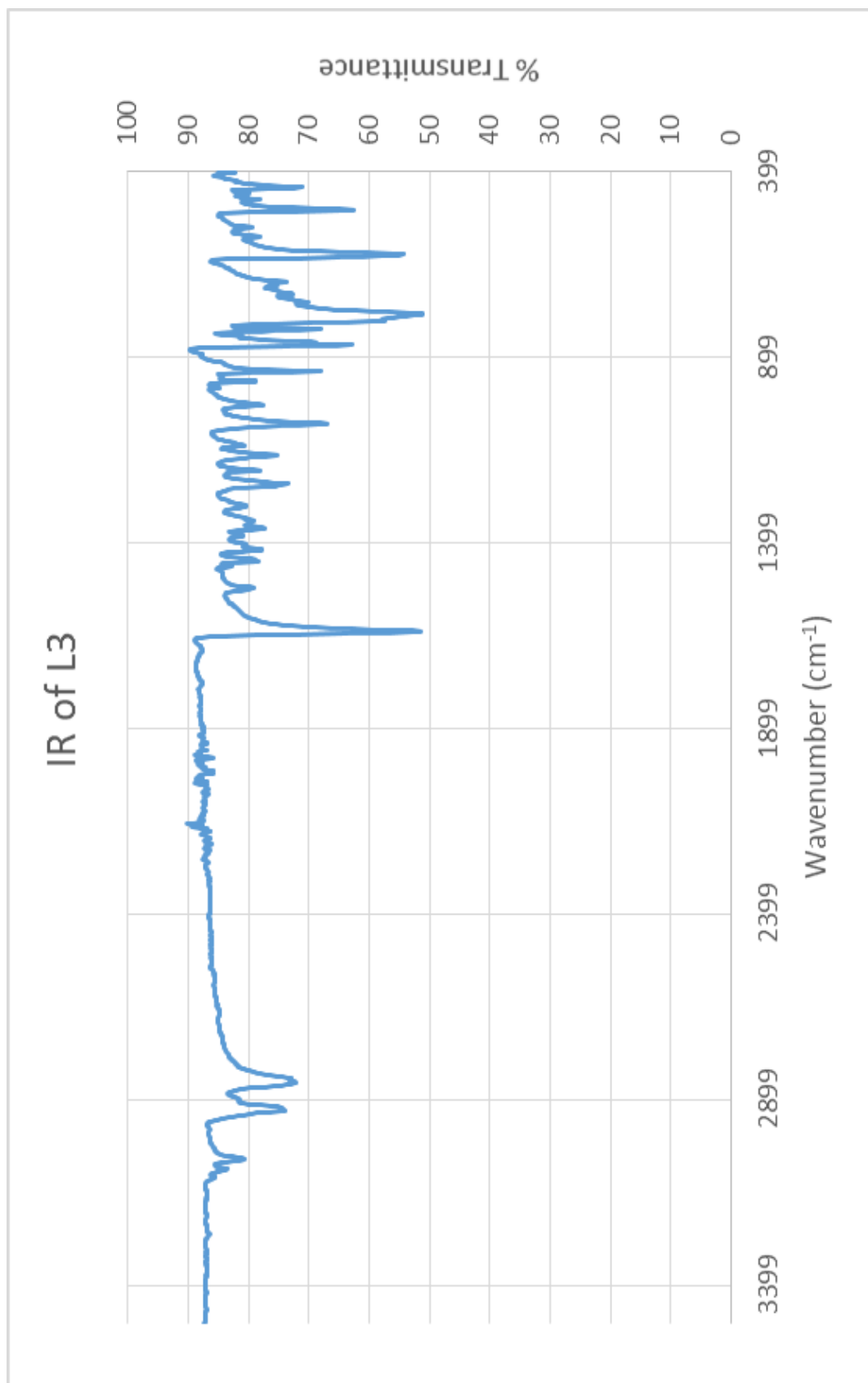
Fluorescence 0.1 mM @ 332 nm

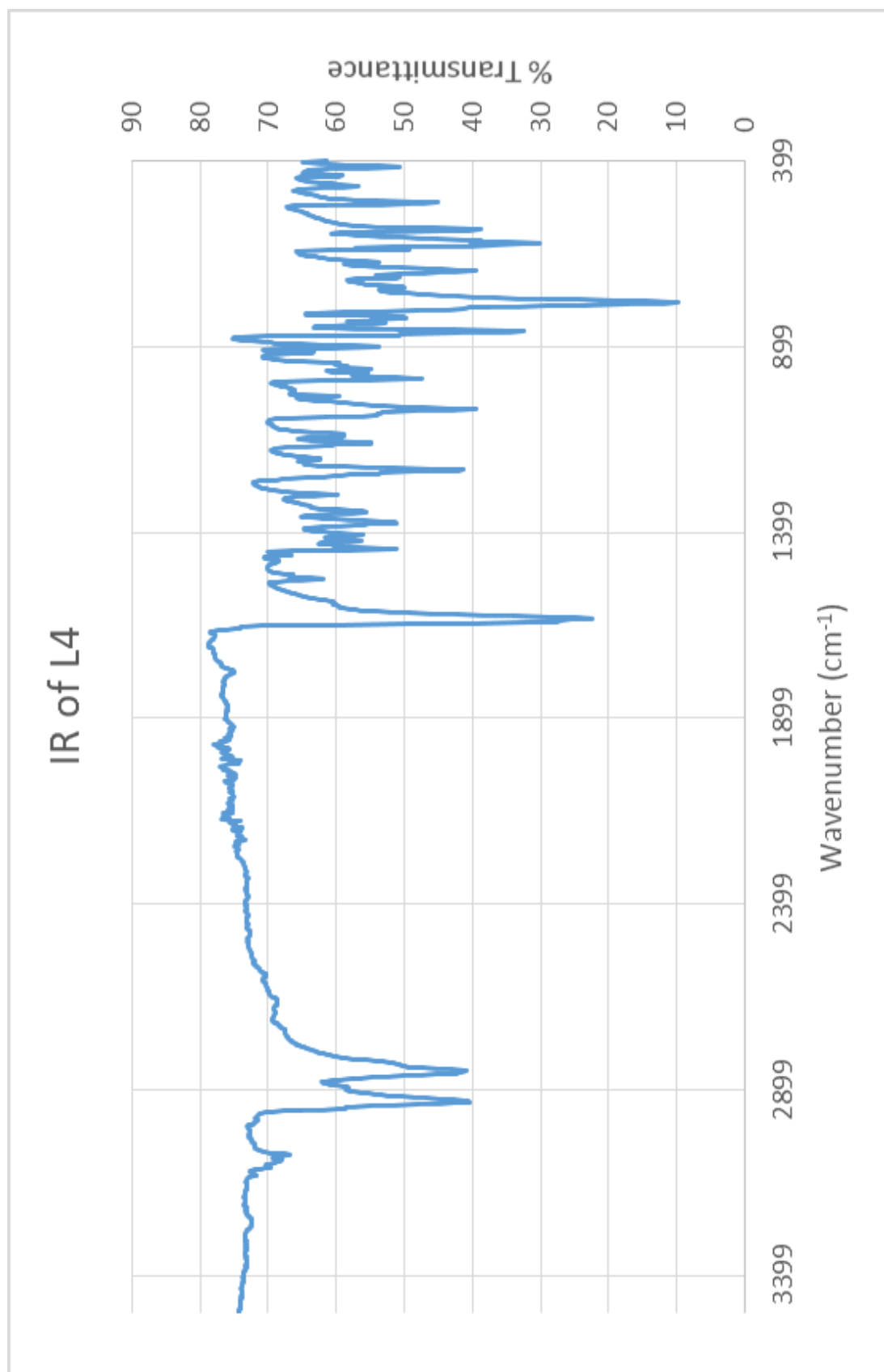




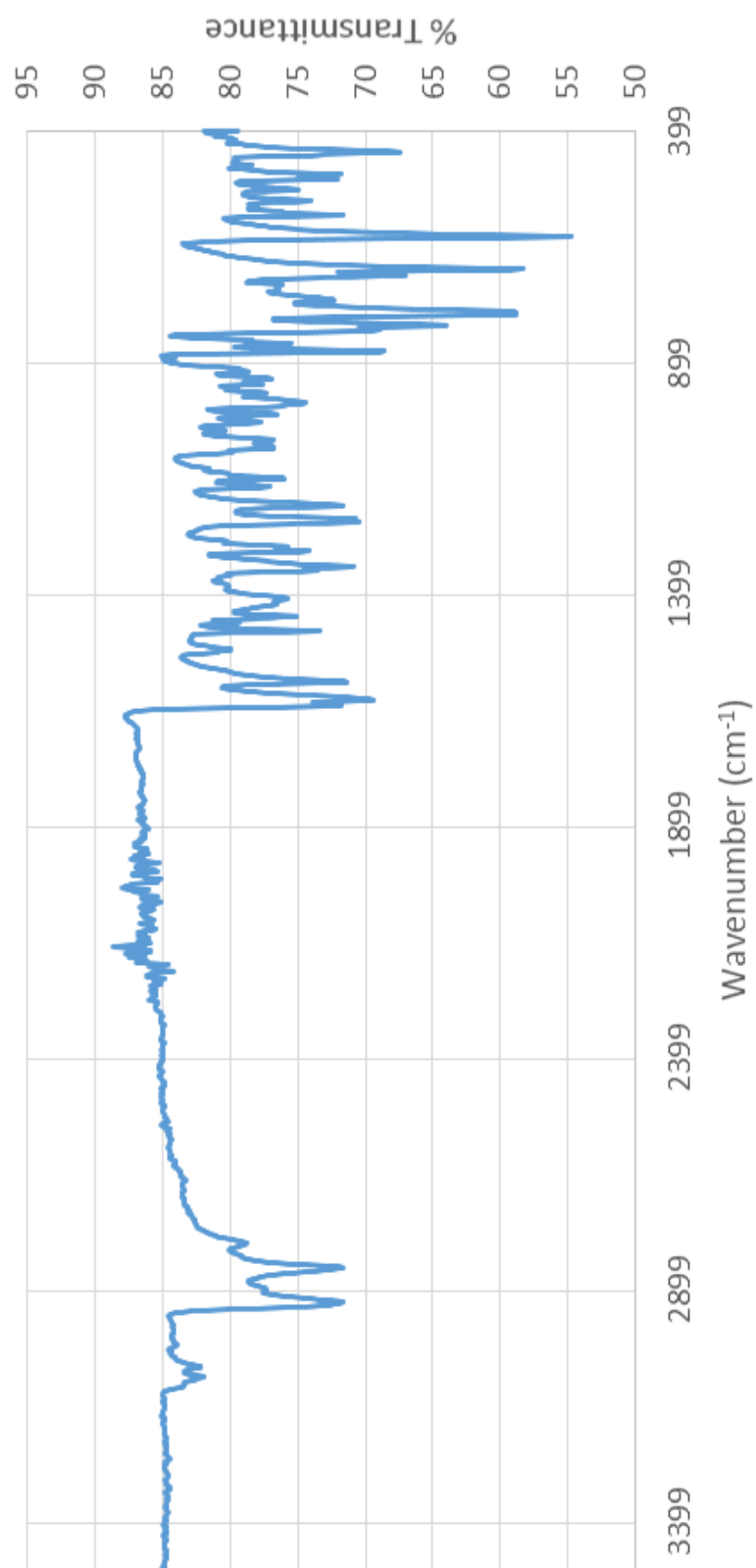
10. Appendix D: IR Spectrum

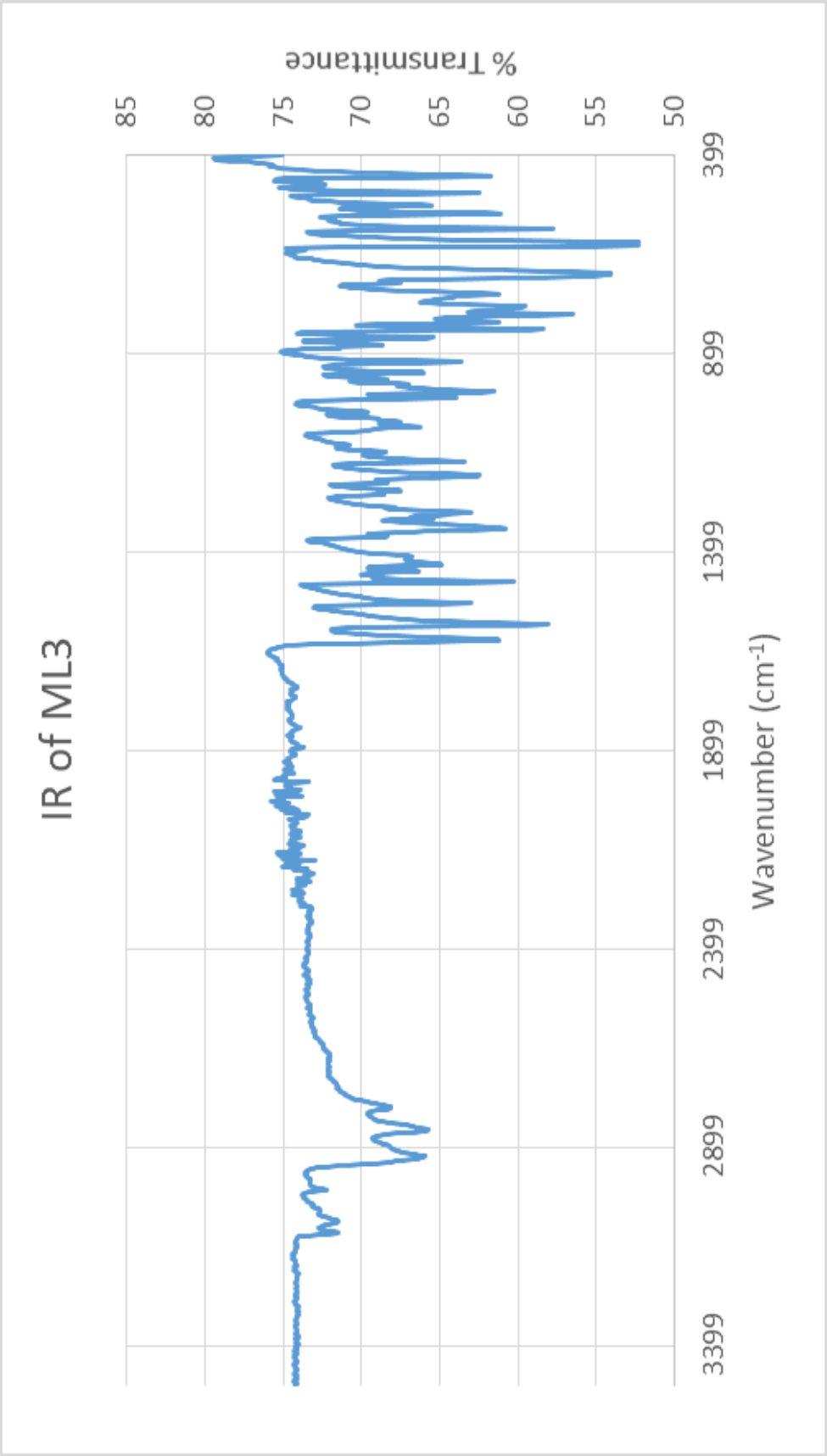




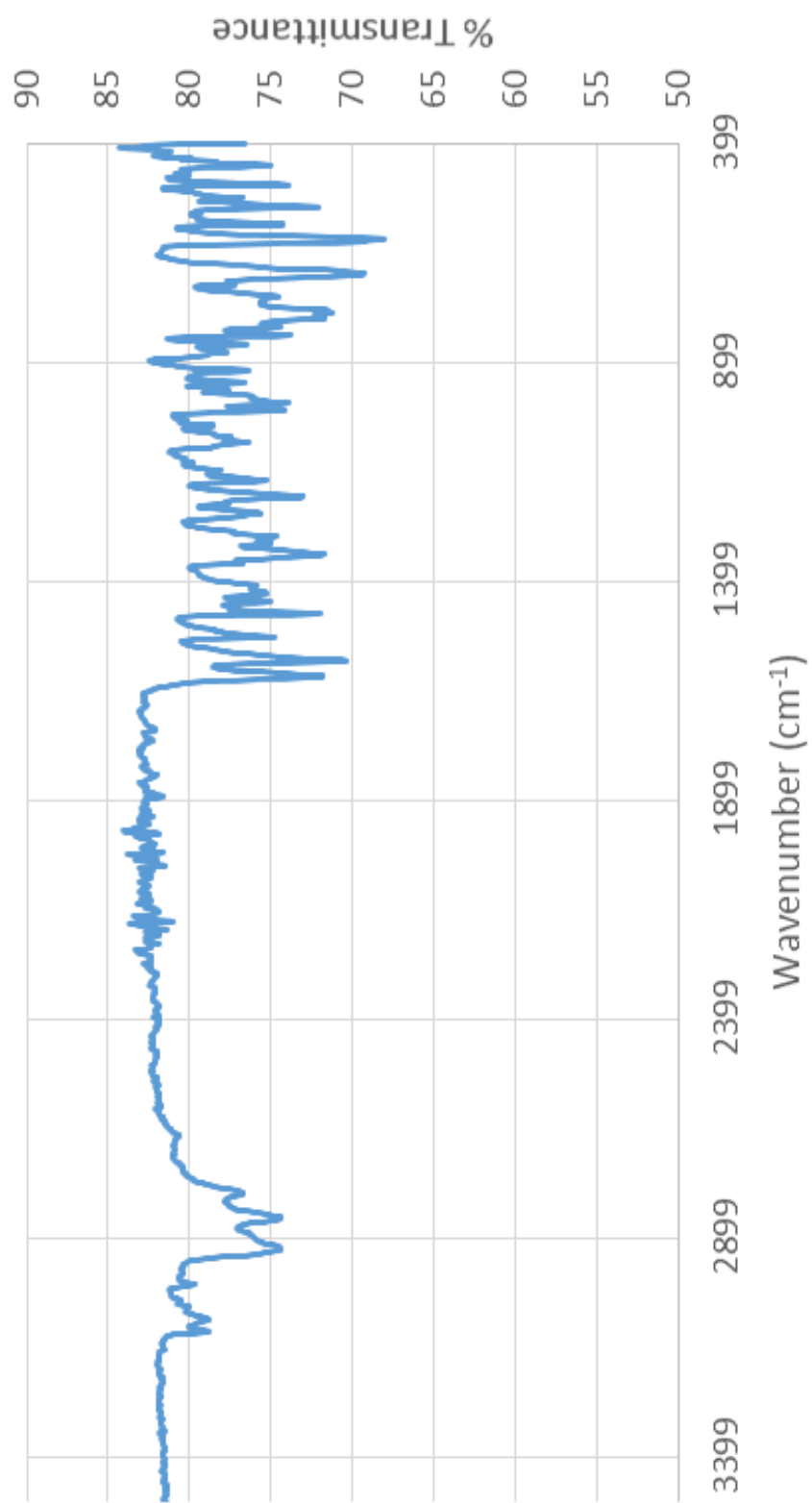


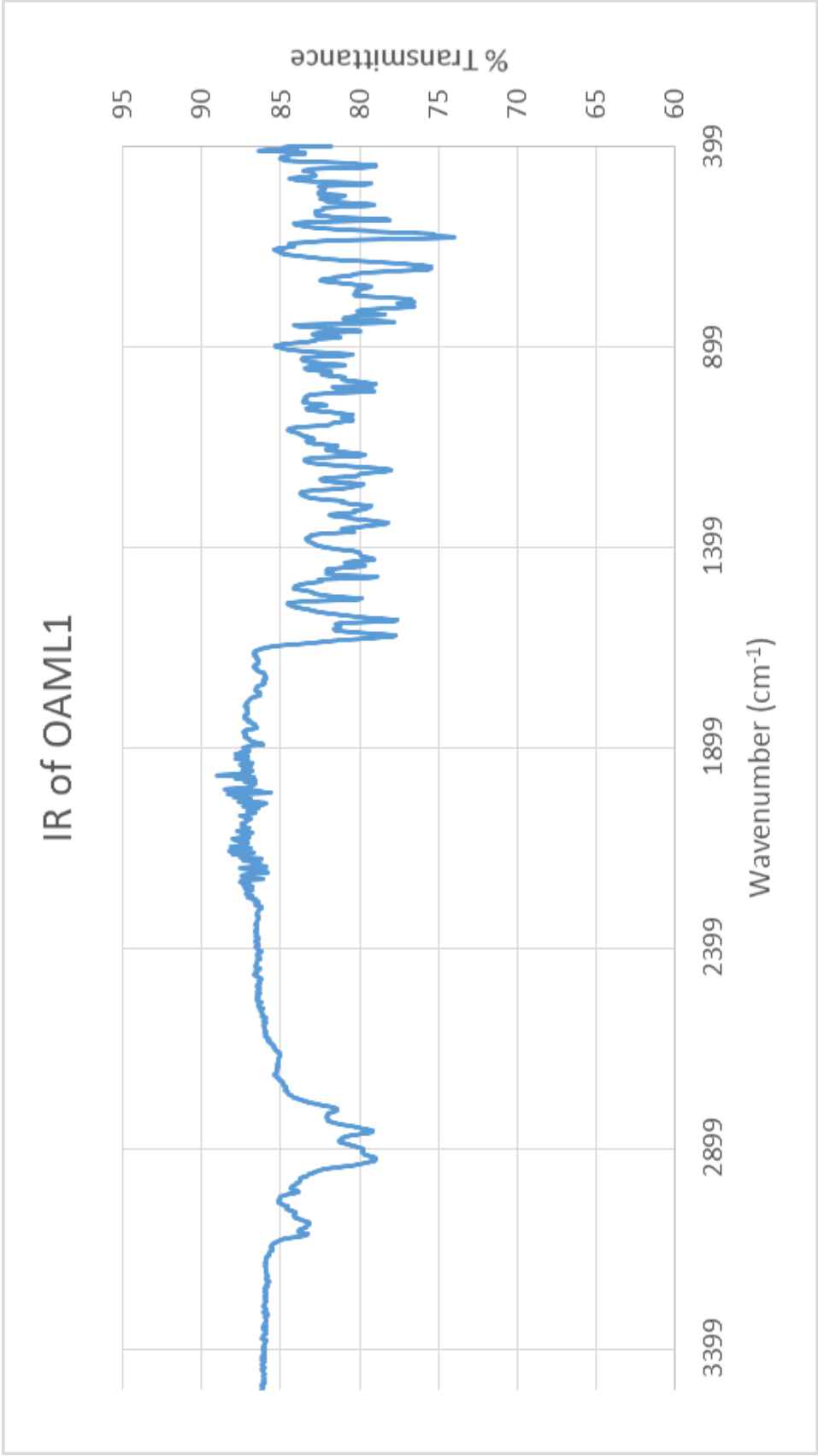
IR of ML1



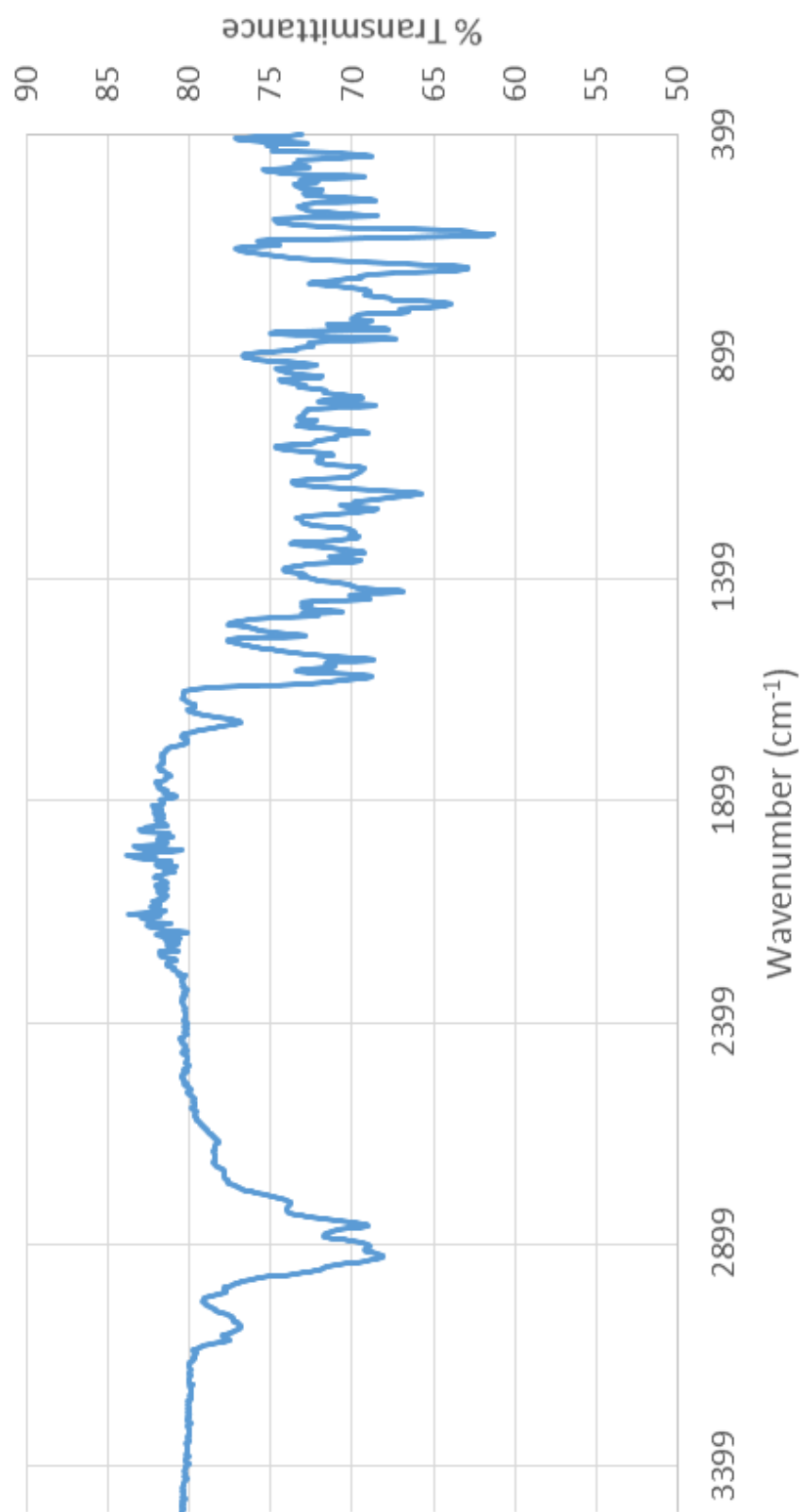


IR of ML4





IR of OAML3



IR of OAML4

